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JOURNAL
OF THE
INDIAN CHEMICAL SOCIETY

VOL. XXXVI OCTOBER, 1959 No. 10

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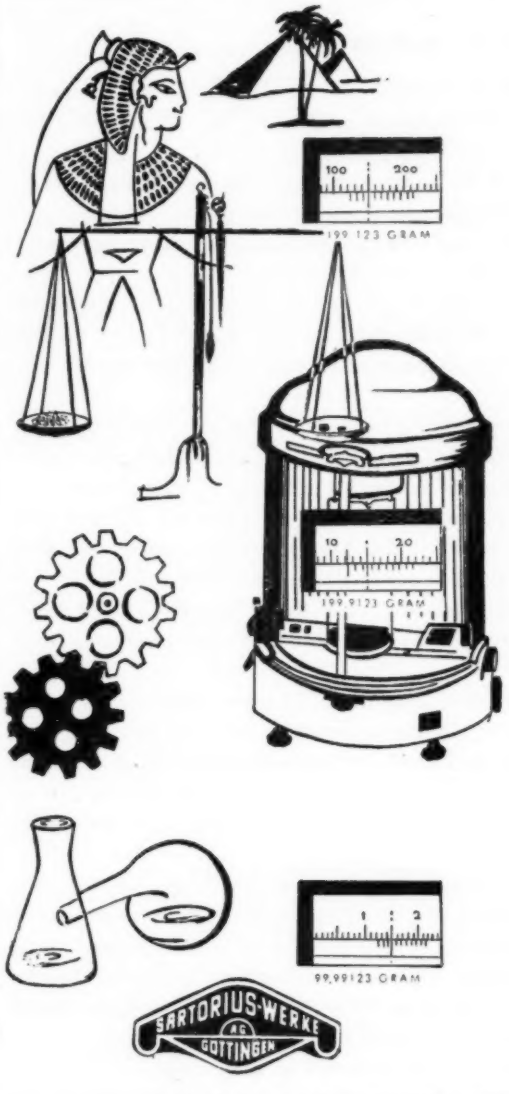

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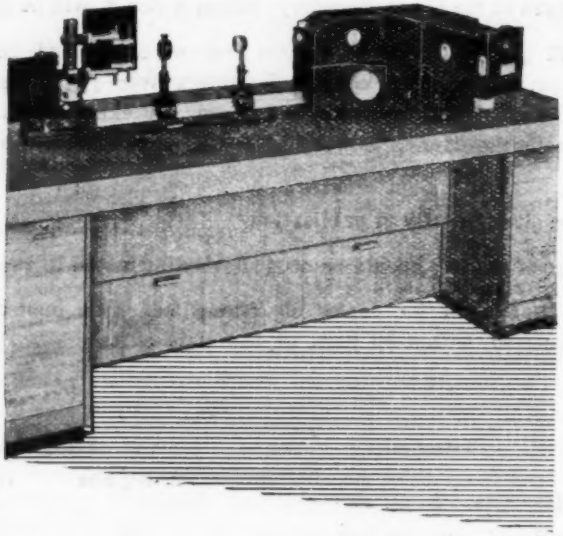

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[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

THE ALKALOIDS OF *RAUWOLFIA CANESCENS* LINN. PART IX. STRUCTURE AND STEREOCHEMISTRY OF RAUWOLSCINE (α-YOHIMBINE)

By Mrs. A. Chatterjee and S. C. Pakrashi*

The complete evidence of the structure and the relative stereochemistry of rauwolscine (XVI), an alkaloid of *Rauwolfia canescens* Linn., have been presented. Elucidation of the stereochemistry of rauwolscine proves its identity with α-yohimbine, establishing simultaneously the steric configuration of the latter, which was not known earlier. C_3-H epimerisation from rauwolscane (*allo*-yohimbanə) (IX) to 3-*epi*-*allo*-yohimbane (3-*epi*-rauwolscane) (IXa), induced by acetic anhydride in presence of base, is also described.

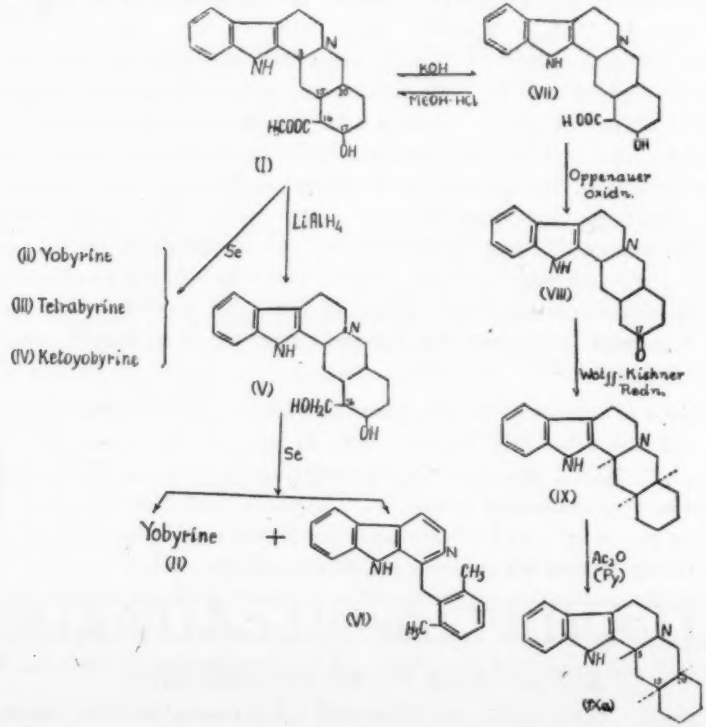
After publication of our results in some preliminary communications on rauwolscine (I), isolated from *Rauwolfia canescens* Linn. (Chatterjee and Pakrashi, *Science & Culture*, 1953, **19**, 109 ; *Naturwiss.*, 1954, **41**, 215 ; *Proc. Indian Sci. Cong.*, 1955, Part III, p. 136 ; Chatterjee, Bose and Pakrashi, *Chem & Ind.*, 1954, 491), as detailed in the present paper, this alkaloid gained tremendous importance for the stereochemical assignment of reserpine, deserpidine and 3-*epi*-α-yohimbine (Chatterjee, Pakrashi and Werner, Zechmeister's "Progress in the Chemistry of Organic Natural Products", Springer-Verlag, Vienna, 1956, Vol. 13, pp. 346-443). The present communication is concerned with several important and new chemical data bearing stereochemical implications in *allo*-yohimbane series, a detailed exposition of experimental evidence of which could not be published earlier because of the long foreign mission (U.S.A.) of one of us (S.C.P.). The paper also describes a novel method for C_3-H epimerisation, induced by acetic anhydride (from *allo*-yohimbane to *epi-allo*-yohimbane) (Chatterjee and Pakrashi, *loc. cit.*, 1955). This procedure is now a stereochemical diagnostic tool in determining the configuration at the asymmetric centre C_3 in *allo*-yohimbane systems. Wenkert and Roychoudhury (*J. Amer. Chem. Soc* , 1958, **80**, 1613) reported recently that they could not reproduce our method for epimerisation, perhaps for the lack of information about the experimental details covered at the end of this paper.

The isolation of keto-yobyrine (IV) from the selenium dehydrogenation of the base (Chatterjee and Pakrashi, this *Journal*, 1954, **31**, 25) and the production of methyl-yobyrine (VI), $C_{20}H_{18}N_2$, m.p. 212-13°, in addition to yobyrine (II) by the selenium dehydrogenation of rauwolscinyl alcohol (V) (Chatterjee and Pakrashi, *loc. cit.*, 1953), $C_{20}H_{20}O_2N_2$, m.p. 226-27°, the lithium aluminium hydride reduction product of rauwolscine, conclusively secured the evidence for its pentacyclic nuclear structure, allocating simultaneously the carbomethoxyl group at C_{16} in ring E of the rauwolscine molecule (I).

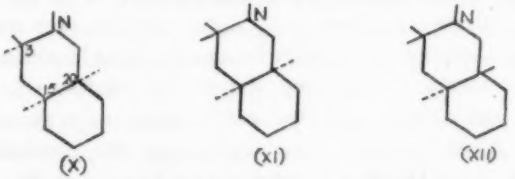
That the hydroxyl group in rauwolscine is secondary and is located at C_{17}, adjacent to the carbomethoxyl group like yohimbine and its stereoisomers (Janot *et al.*, *Bull. Soc.*

* Present address : Indian Institute for Biochemistry & Experimental Medicine, Calcutta.

Chim., 1952, **19**, 1085), were demonstrated (Chatterjee and Pakrashi, *loc. cit.*, 1953) by the Oppenauer oxidation of rauwolscine or better rauwolscinic acid (VII) [Chatterjee (Ne'e Mookerjee), this *Journal*, 1941, **18**, 33, 485] to a decarboxylated ketone, rauwolscone (*allo*-yohimbone) (VIII), $C_{19}H_{22}ON_2$, m.p. 230-31°. The hydroxyl group in rauwolscine reacted with sulphuric acid to form a sulphuric ester, $C_{21}H_{26}O_6N_2S$, m.p. 262-63°, but the latter on treatment with alkali liberated rauwolscinic acid and not *apo*-rauwolscine although such difficulty was not encountered in obtaining *apo*-yohimbine from yohimbine under the same experimental conditions, thus pointing out an essential difference in orientation of the hydroxyl groups in these two alkaloids. Rauwolscone, the carbomethoxyl-free compound, upon the Huang-Minlon modification of the Wolff-Kishner reduction, yielded rauwolscane (*allo*-yohimbane) (IX), $C_{19}H_{24}N_2$, m.p. 156-57°, which adduced information necessary for stereochemical assignment at the asymmetric centres C_3, C_{15} and C_{20}. Both rauwolscine and *allo*-yohimbine on saponification and subsequent esterification with methanolic hydrogen chloride regenerated the original bases (Chatterjee and Pakrashi, *loc. cit.*, *Naturwiss*, 1954; Le Hir *et al.*, *Bull. Soc. Chim.*, 1953, **20**, 1027) which settled the configuration of the carbomethoxyl group in both the alkaloids as equatorial. Therefore these two bases are C_{17} and not the C_{17}-epimers, as was beleived by Le Hir *et al.*, *loc. cit.*) at that time. Consequently, rauwolscine should be identical with α-yohimbine *, which was found to be the case (Chatterjee, Bose and Pakrashi, *loc. cit.*).



Thus, identity of rauwolscane with *allo*-yohimbane firmly established the all-*syn* configuration (X) of rauwolscine (α-yohimbine)* (Le Hir *et al.*, *loc. cit.*) at C_3, C_{15} and C_{20} and not the *anti-syn* (XI) (Janot *et al.*, *Helv. Chim. Acta*, 1955, **38**, 1073), and the saponification experiment proved equatorial orientation of the carbomethoxyl function (C_{16}) in both rauwolscine and *allo*-yohimbine. This is the first rigorous proof of the relative stereochemistry of rauwolscine and *allo*-yohimbine at the four asymmetric centres at C_3, C_{15}, C_{16} and C_{20}. These have been further corroborated by acetylation experiments (Chatterjee and Pakrashi, this *Journal*, 1954, **31**, 29) as would be evidenced from the discussions in the sequel. Both *allo*-yohimbine and rauwolscine yield an *O*-monoacetyl derivative whereas yohimbine under similar reaction conditions produces *O*:*N*-diacetyl as well as *O*-monoacetyl compounds (Schömer, *Arch. Pharm.*, 1927, **265**, 517). The failure to obtain the diacetyl derivative from the former two alkaloids was ascribed tentatively to their steric configuration (X). This speculative assumption was subsequently substantiated from molecular model experiments (Chatterjee *et al.*, *loc. cit.*, 1954). The latter showed that in all *-syn* (X) or all *-anti* (XII) configurations, the NH group would be considerably hindered sterically for acylation, whereas in the *anti-syn* structure (XI), such substitution would not be impossible provided that the carbomethoxyl group at C_{16} is equatorial. Hence, *allo*-yohimbine and rauwolscine must have the all-*syn* structure (X) since according to our prediction, 3-*epi*-α-yohimbine, which produces both the di- and mono-acetyl derivatives, should have the *anti-syn* (XI)



(X) (XI) (XII)

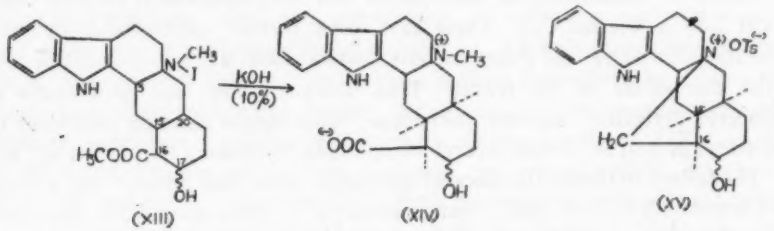
configuration. In conformity with our prediction, the isomer with the *anti-syn* (XI) configuration, 3-*epi*-α-yohimbine, was later found to produce both the di- and mono-acetyl derivatives (Bader *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 3547). It now remains to be seen whether our second prediction, viz., ψ-yohimbine with all-*anti* (XII) configuration affords only *O*-monoacetyl derivative unlike yohimbine (*vide supra*).

Our conclusions regarding the configuration (relative stereochemistry) of rauwolscine and, hence, *allo*-yohimbine, at the four asymmetric centres C_3, C_{15}, C_{16} and C_{20} have received independent confirmation from the known relationship between reserpine, 3-*epi*-α-yohimbine, and rauwolscine (Macphillamy *et al.*, *ibid.*, 1955, **77**, 4335).

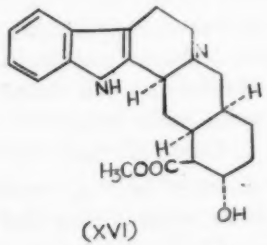
It is, however, interesting to note in this connection that a significant piece of evidence reported [Chatterjee (Ne'e Mookerjee), this *Journal*, 1951, **28**, 29] as far back as in 1951 went unnoticed. It was observed that rauwolscine methoiodide (XIII), m.p. 268°, when treated with 10% aqueous caustic potash, produced a hygroscopic betaine, *iso*rauwolscine (XIV) which was only stable as salts. The formation of this betaine

* Though α-yohimbine was first isolated (Lillig, *Merck's Jahrb.*, 1928, **42**, 20) from other sources, rauwolscine [Chatterjee (Ne'e Mookerjee), this *Journal*, 1941, **18**, 33; 1946, **23**, 6) represents the first recognition of the yohimbine skeleton in *Rauwolfia* alkaloids. Since their identity has been proved and the workers in the field freely use both the names, it is proper that the name, rauwolscine, should be retained in parenthesis to avoid confusion, particularly with reference to the latter class of alkaloids.

leads to the conclusion that the orientation of the carbomethoxyl group at C_{16} with respect to the C_{15} and C_{20} hydrogen atoms must be *trans*-, while the relationship between the latter two would be *cis*- [cf. the quaternary compound (XV) obtained by the tosylation of reserpinol] (Diassi, *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 4687; van Tamelen and Hance, *ibid.*, 1955, **77**, 4335).



Although the following facts, viz., (*a*) the reluctance of rauwolscine towards acid-catalysed dehydration (Chatterjee and Pakrashi, *loc. cit.*, 1953), (*b*) the difficulty of chromic acid oxidation of rauwolscine (as well as yohimbine) by the method of Sarett *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 1707), (*c*) easy *O*-acetylation (Chatterjee and Pakrashi, *loc. cit.*, this *Journal*, 1954) and (*d*) the failure to isolate any isomeric base from the equilibration reaction of rauwolscine (Chatterjee and Pakrashi, unpublished) in presence of sodium methoxide in diethyleneglycol for 16 hours pointed to the equatorial nature of the C_{17} hydroxyl group (Barton, *J. Chem. Soc.*, 1953, 1927) in rauwolscine, we had to sacrifice all these chemical evidences (negative for axial hydroxyl function) in favour of the more positive physical evidence, *i.e.* infra-red spectra, to postulate the C_{17} hydroxyl in rauwolscine as axial, and consequently that in *allo*-yohimbine as equatorial (Chatterjee, Bose and Pakrashi, *Chem. & Ind.*, 1954, 491). On the circumstantial evidences (Huebner *et al.*, *Exper.*, 1955, **11**, 303; *J. Amer. Chem. Soc.*, 1955, **77**, 5725; Woodward *et al.*, *ibid.*, 1956, **78**, 2023, 2657; *Tetrahedron*, 1958, **2**, 1) it appeared the other way around. The pertinent direct chemical evidence was lacking so far to decide between these two alternatives. Conclusive proof has recently been adduced (Le Hir and Warnhoff, *Compt. rend.*, 1958, **246**, 1564) in favour of the equatorial hydroxyl in rauwolscine and axial in *allo*-yohimbine by direct conversion of the latter to the former by equilibration in benzene solution in presence of potassium butoxide[t]. It might be noted in this connection that the formation of *apo*-rauwolscine from rauwolscine (Wenkert and Roychoudhury, *loc. cit.*) by tosylation, followed by the collidine detosylation (private communication in our laboratory from Prof. E. Schlittler, Ciba, Summit, N. Y., U. S. A.), involves 1:2 *cis*-elimination. Such dehydration is not surprising in systems like rauwolscine (Barton and Cookson, *Quart. Revs.*, 1956, **10**, 66 and the references cited therein). On the basis of these observations and combining all the chemical and physical (molecular rotation differences coupled with the conformational analyses) evidences (as summarised in a recent publication by Bose *et al.*, *Indian J. Pharm.*, 1956, **18**, 185 and the references cited therein), the relative and the absolute configuration of rauwolscine (α-yohimbine) can be written as (XVI), and *allo*-yohimbine as it C_{17}-epimer.



(XVI)

As a result of our molecular model experiments (*loc.cit.*), it was further observed that in rauwo scine and *allo*-yohimbine, the *N*-acylation would only be hindered due to the equatorial carbomethoxyl group at C_{16}, but also the axial hydrogen at C_{14} would be expected to exert some hindering effect. To resolve the question as to which of them is more responsible for such hindrance, *N*-acetylation experiment of rauwolscane (*allo*-yohimbane), which is free from carbomethoxyl and hydroxyl groups, was tried. The oxygen-free base was refluxed for 15 hours or more with acetic anhydride in presence of pyridine or fused sodium acetate. To our surprise, instead of the expected product (*N*-acylrauwolscane), 3-*epi-allo*-yohimbane (IXa) (Stork and Hill, *J. Amer. Chem. Soc.*, 1954, **76**, 949), m.p. 211-12°, was obtained in 16% yield along with the major part of the starting material (Chatterjee and Pakrashi, *loc.cit.*, 1955). The important bearing of this observation, *i.e.*, the acid-catalysed or acetic anhydride-induced C_3-epimerisation from the more stable *allo*-yohimbane derivative to its less stable C_3-epimer, was apparent later on, viz., in the determination of the stereochemistry of reserpine (Macphillamy *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 4335 ; Huebner *et al.*, *Exper.*, 1955, **11**, 303 ; Wenkert and Liu, *ibid.*, 1955, **11**, 302 ; Huebner, *Chem. & Ind.*, 1955, 1186). It may be recalled that rauwolscine itself under the same acetylation conditions affords *O*-monoacetylrauwolscine (Chatterjee and Pakrashi, this *Journal*, 1954, **31**, 29) in good yield. This is in keeping with the observation (Macphillamy *et al.*, *loc. cit.*) that unlike the normal and ψ-yohimbines, conversion of *allo-* to *epi-allo* system or *vice versa* is a function of the ring E substituents on which the direction of the equilibrium depends due to the small energy barrier between the latter two forms.

EXPERIMENTAL*

Isolation of the Minor Products of Selenium Dehydrogenation of Rauwolscine.—Rauwolscine (4.5 g.) was subjected to the selenium dehydrogenation by the usual method (Chatterjee and Pakrashi, *loc. cit.*, p. 25) and extracted with benzene. The concentrated extract on cooling overnight in a frigidaire deposited yobyrine (*loc.cit.*) that was filtered off. The filtrate was reduced to a small volume (25 c.c.) and chromatographed thrice in a column (32 × 1.7 cm) over alumina, and eluted with benzene. Of the 25 fractions, the first ten were collected in 25-30 c.c., next five in 50 c.c. and then 75 c.c.

* All melting points are uncorrected. Brockmann alumina, activity I, was used throughout. Analyses were done by Messrs. G. Weiler & F. Strauss, Oxford, England and Mrs. Chhabi Dutta of the University College of Science, Calcutta.

(*i*). *Tetrahydroisoyobyrine* ("*Tetrabyrine*") (III).—The fractions (1-3) yielded a red oil which on chromatography over alumina and crystallisations from ethyl alcohol afforded stout rods, m.p. 164-65°. It showed no depression in the melting point when mixed with the "tetrabyrine" (Wibaut and van Gastel, *Rec. trav. chim.*, 1935, **54**, 85), obtained from yohimbine by the same procedure. (Found: C, 82.59; H, 7.21; N, 10.21. Calc. for $C_{19}H_{20}N_2$: C, 82.60; H, 7.24; N, 10.14%).

(*ii*). *Yobyrine* (II).—The fractions (4-9) on purification afforded needles, m.p. 206-208°, crystallising out of aqueous methanol, identified as yobyrine by direct comparison (Chatterjee and Pakrashi, *loc.cit.*).

(*iii*). *Keto-yobyrine* (IV).—The rechromatography of the fractions (13-22) was followed by the conspicuous bluish green fluorescence, while the column became yellow. On evaporation of the eluate and several recrystallisations of the residue from benzene, yellow needles were obtained, m.p. 316-18° (decomp.). It was proved to be keto-yobyrine (Wibaut and van Gastel, *loc. cit.*) by comparison with a sample prepared from yohimbine under the identical conditions in our laboratory. (Found: C, 80.24; H, 5.45; N, 9.36. Calc. for $C_{20}H_{16}ON_2$: C, 80.00; H, 5.33; N, 9.33%).

$LiAlH_4$ *Reduction of Rauwolscine*: *Preparation of Rauwolscinyl Alcohol* (V).—A solution of pure and well-dried rauwolscine (0.5 g.) in dry tetrahydrofuran (6 c.c.) was added dropwise to a well-cooled suspension of $LiAlH_4$ (0.2 g.) in the same solvent (10 c.c.) with constant stirring. After the addition was over, the stirring was continued for 4 hours more in the cold. The complex was decomposed with a little watter (4-5 c.c.) and stirred again in the cold for an hour, filtered and the solvent removed under reduced pressure. The residue was taken up in ether, washed, dried and the solvent evaporated. The glassy mass yielded yellow rods (0.35 g.), m.p. 183° (from acetone) which on recrystallisation from ethyl acetate and acetone (2:1), followed by the chromatography over alumina using the same solvent mixture (1:1) as the eluent and further crystallisation from acetone, yielded colorless stout rods of pure rauwolscinyl alcohol (0.3 g.). It retained the solvent of crystallisation which was easily lost when dried over P_2O_5 at 130-40°/10 mm. The dried sample melts at 225-27°. It is soluble in ethyl and methyl alcohols and benzene. Methoxyl estimation showed negative results. (Found: C, 73.60; H, 8.24; N, 8.71. Calc. for $C_{20}H_{26}O_2N_2$: C, 73.61; H, 7.97; N, 8.58%).

Attempted preparation of hydrochloride or sulphate failed due to the extreme hygroscopic nature of the salts. The picrate separated from alcohol-acetone solution as an orange-yellow amorphous solid, m.p. 216-17° (decomp.). (Found: N, 12.74. Calc. for $C_{26}H_{29}O_9N_5$: N, 12.61%).

The styphnate was obtained as a deep red amorphous mass from ethyl alcohol which decomposed above 300° without any definite melting point. (Found: N, 12.36. Calc. for $C_{26}H_{29}O_{10}N_5$: N, 12.25%).

Selenium Dehydrogenation of (V).—Rauwolscinyl alcohol (1.0 g.) was dehydrogenated with black pulverised selenium (1.0 g.) at 300° as in the case of rauwolscine. After extraction of the products with benzene for 16 hours and removal of the solvent, the residue was distilled in high vacuum, when a yellow oil distilled at 165-

70°/0.005 mm, which solidified on cooling. Attempted crystallisation from methanol yielded a mixture of products as a light yellow amorphous mass, m.p. 208-12°. It was chromatographed in a column (32 × 1.7 cm) over alumina using benzene as eluent. The first ten fractions were collected in 10 c.c., next five in 25 c.c., and the rest in 30 c.c. The fractions (2-6) partly solidified as a glassy mass and on keeping in air as needles, m.p. 110-15°. It was not characterised further.

The crystalline material obtained in fractions (9-12), on several recrystallisations from methyl alcohol, yielded shining colorless prisms of methylyobyrine, m.p. 213-14° (without decomp.) (lit., m.p. 218°), identified by direct comparison with an authentic sample prepared from yohimbyl alcohol according to Karrer *et al.* (*Helv. Chim. Acta*, 1952, **35**, 865). (Found: C, 84.06; H, 6.29; N, 9.6. Calc. for $C_{20}H_{18}N_2$: C, 83.9; H, 6.29; N, 9.79%).

The hydrochloride crystallised from alcohol (violet fluorescence) in needles, m.p. 286-88° (decomp.). The picrate was obtained from absolute alcohol in long needles in clusters, m.p. 241-42° (decomp.). It depressed the melting point of the yobyrine picrate (Chatterjee and Parkashi, *loc. cit.*), m.p. 239° (decomp.) by 30°. (Found: N, 13.61. Calc. for $C_{20}H_{21}O_7N_5$: N, 13.59%).

Oppenauer Oxidation of Rauwolscinic (α-*Yohimbic*) *Acid* (VII): *Preparation of Rauwolscone Hydrochloride and Rauwolscone* (allo-*Yohimbone*) (VIII).—The procedure followed by Janot *et al.* (*loc. cit.*) was modified. Rauwolscinic acid [Chatterjee (Née Mookerjee), this *Journal*, 1941, **18**, 33, 485] (4.0 g.) was refluxed for an hour in dry xylene (400 c.c.), a portion (200 c.c.) of which was distilled off under reduced pressure at 90-100°. Freshly distilled *cyclo*hexanone (125 c.c.) and freshly prepared and desiccated aluminium phenoxide (24.0 g.) were added to it. The mixture was refluxed for 48 hours at 155-65° in an oil-bath in an atmosphere of nitrogen. After cooling and washing with 2*N* sodium carbonate solution, then with water, the organic layer was diluted with ether (300 c.c.) and extracted with 2*N*-HCl (5 × 150 c.c.). Basification and re-extraction of the ethereal layer with the same acid solution furnished shining needles of rauwolscone hydrochloride (1.4 g.), m.p. 286-87° (decomp.). The melting point did not change on further purification. It was filtered and the norite-treated mother-liquor on basification liberated rauwolscone (1.2 g.). The crude ketone was distilled at 200-20°/0.005 mm and the resultant heavy oil was crystallised from methanol in colorless needles, m.p. 230-31° (decomp.), $[\alpha]_D^{28}$, -128° (Py). The infra-red seectrum showed bands at 5.89 μ (cyclic ketone), 2.89 μ (:NH) while the bands at 2.8 μ and 9.9 μ (-OH) were absent. The base did not show any characteristic colour with alcoholic ferric chloride solution. It was also free from methoxyl group. (Found: C, 76.90; H, 7.02; N, 10.30. Calc. for $C_{19}H_{22}ON_2$: C, 77.55; H, 7.48; N, 9.52%).

Rauwolscone picrate crystallised from absolute alcohol in needles, m.p. 208-209° (decomp.). (Found: N, 12.64. Calc. for $C_{25}H_{25}O_8N_5.H_2O$: N, 12.94%). The orange D.N.P.H. of the ketone melted at 260-62° (decomp.).

Wolff-Kishner Reduction of Rauwolscone (VIII): *Preparation of Rauwolscane* (allo-*Yohimbane*) (IX).—Following essentially the conditions used by Janot *et al.*

(*loc. cit.*, 1952), the reduction product of rauwolscone (0.43 g.) was taken up in ether (3 × 100 c.c.); the ether layer was washed with water and extracted with 2*N*-HCl (3 × 75 c.c.). The acid extract was heated on a water-bath, cooled and filtered. The granular product (0.32 g.) on crystallisation from absolute alcohol yielded white shining flakes of rauwolscane hydrochloride, m.p. 281-82° (decomp.). The aqueous solution of the hydrochloride was treated with norite and the cooled solution was basified with sodium carbonate. The precipitate was allowed to stand in an ice-bath for 3 hours and filtered. A further amount was likewise recovered from the mother-liquor of the hydrochloride. The total product was chromatographed through alumina using benzene-petroleum-ether (8 : 2) as eluent. Recrystallisation from methyl alcohol yielded white shining stout rods of rauwolscane, m.p. 156-57°, $[\alpha]_D^{28}$ -168° (Py), while crystallisation from acetone afforded transparent quadrangular plates required for the X-ray study (Ray, *Science & Culture*, 1955, **20**, 507; *Acta Cryst.*, 1956, **9**, 199). The acetone of crystallisation is easily lost, resulting in an opaque mass. The infra-red spectrum in chloroform showed complete absence of the band at 5.89 μ (>C=O). (Found: C, 80.63; H, 8.40; N, 10.00. Calc. for $C_{19}H_{24}N_2$: C, 81.43; H, 8.57; N, 10.00%).

The orange-red rauwolscane picrate, m.p. 230°, was prepared and crystallised in needles from alcoholic solution. (Found: N, 13.70. Calc. for $C_{25}H_{27}O_7N_5$: N, 13.75%).

Attempted Acetylation of Rauwolscane (IX): *Preparation of* 3-epi-allo-*Yohimbane* (IXa) *from Rauwolscane.*— (*a*). Rauwolscane (0.16 g.) was dissolved in acetic anhydride (5 c.c.) to which fused sodium acetate (0.16 g.) was added and the mixture refluxed for 10 hours at 140-50° or better, (*b*) the compound (0.5 g.) in acetic anhydride (10 c.c.) was refluxed for 15 hours in presence of pyridine (5 drops) and worked up as usual. The crude product was chromatographed in a column (22 × 1.7 cm) over alumina and fractions were collected in 10 c.c. portions. Most of the unchanged rauwolscane (80%) was eluted in the early fractions with benzene-petroleum ether (8 : 2), followed by a second product eluted with benzene-acetone (8 : 2). Benzene-acetone eluents from (*b*) (0.08 g., 16%) were chromatographed and recrystallised from benzene-petroleum ether (8 : 2) as colorless needles in clusters (0.04 g.) or from methyl alcohol in silky flakes, m p. 211-12°. It was proved to be 3-*epi-allo*-yohimbane (3-*epi*-rauwolscane) (Stork and Hill, *J. Amer. Chem. Soc.*, 1954, **76**, 949). No acetyl was found by analysis. (Found: C, 81.19; H, 8.49; N, 9.91. Calc. for $C_{19}H_{24}N_2$: C, 81.43; H, 8.57; N, 10.00%).

The authors express their sincere thanks to the West Bengal Government for financial support. Their thanks are also due to Prof. L. Zechmeister, California Institute of Technology, for the analysis of 3-*epi-allo*-yohimbane, and to Dr. H. N. Khastgir and Dr. R. K. Neogy for the infra-red spectra.

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Received April 27, 1959.

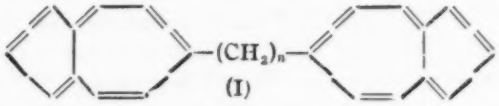
[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

AZULENES AND RELATED SUBSTANCES. PART X*. A NEW ROUTE TO AZULENES: SYNTHESIS OF 6-METHYLAZULENE

By Sukh Dev

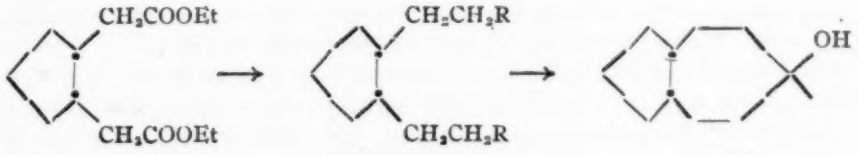
A new route to bi*cyclo*-(o :3 :5)-decane system, involving a 'Grignard ring-closure', is described.

As a preliminary to the synthesis of azulene derivatives of type (I):

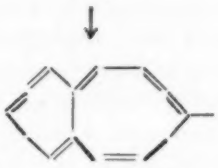


(I)

a method capable of being extended to such systems has been developed, and is illustrated below for the preparation of 6-methylazulene (VII):



(II) (III: R= OH) (IV: R= Br) (V : R= MgBr) (VI)



(VII)

Lithium aluminium hydride reduction of diethyl *cis-cyclo*pentane-1 : 2-diacetate (II) afforded the glycol (III) in 95% yield ; (III) had been prepared previously (Plattner and Studer, *Helv. Chim. Acta*, 1946, **29**, 1432) by the Bouveault-Blanc reduction of (II) in a poor yield only. Action of phosphorus tribromide on the glycol furnished the dibromide (IV), and the Grignard reagent derived from this underwent cyclisation on treatment with ethyl acetate under high dilution conditions to afford 4-methyl-*cis*-bi*cyclo*-(o : 3 : 5)-decan-4-ol (VI) in a poor yield only. The crude carbinol was dehydrated with potassium hydrogen sulphate and the resulting olefin on sulphur-dehydrogenation yielded 6-methylazulene, which had been prepared previously by other workers (Sôrm and Fajkos, *Coll. Czech. Chem. Comm.*, 1947, **12**, 81 ; Hafner, *Angew. Chem.*, 1955, **67**, 302 ; Plattner and Studer, *loc. cit.*) by different methods.

* Experimental

Diethyl cis-cyclo*Pentane*-1 : 2-*diacetate* (II).—A mixture of *cis-cyclo*pentane-1 : 2-diacetic acid (18.6 g.) (Sukh Dev, this *Journal*, 1953, **30**, 815), ethanol (30 c.c.), thiophene-free benzene (40 c.c.) and H_2SO_4 (conc., 5 c.c.) was refluxed for 15 hours and then worked up to yield the ester as a colorless liquid (23-24 g., 95-98%), b.p. 139°/4 mm, 126°/1 mm, n_D^{25} 1.4513-1.4515.

ββ'-(cis-cyclo*Pentane*-1 : 2)-*diethanol* (III).—To a stirred and ice-cooled suspension of $LiAlH_4$ (5.7 g., 0.15 *M*) in ether (125 c.c.) a solution of the above ester (23 g., 0.095*M*) in 50 c.c. ether was let in during half-an-hour. After stirring for another hour at ice-temperature, the mixture was left aside at room temperature for 15 hours, and then finnally refluxed for 2 hours. Excess of the hydride was destroyed at -5 to -10° by ethyl acetate (15 c.c.), and then the complex decomposed with ice-cold 15% H_2SO_4 (125 c.c.). The ether layer was separated, the aqueous portion diluted with water, saturated with ammonium sulphate, and extracted with ether (50 c.c. × 3). The combined ether extract was washed successively with saturated aqueous ammonium sulphate and saturated $NaHCO_3$ solution and dried. The solvent was flashed off and the residue fractionated to furnish the glycol as a colorless, viscous liquid, b.p. 153°/2 mm, n_D^{25} 1.4838, yield 14.2 g. (94%). (Found: C, 68.40; H, 11.18. $C_9H_{18}O_2$ requires C, 68.35; H, 11.39%).

bis-3 : 5-*Dinitrobenzoate* was crystallised from benzene-hexane in white buttons, m.p. 140-41°. (Found: N, 10.28. $C_{23}H_{22}O_{12}N_4$ requires N, 10.25%).

ββ'-(cis-cyclo*Pentane*-1 : 2)-*diethyl Bromide* (IV).—The above glycol (9.5 g, 0.06 *M*) was suspended in benzene (30 c.c.) containing one drop of anhydrous pyridine and to it PBr_3 (10.84 g., 0.04 *M*) was added dropwise at 0°. The reaction mixture was stirred at ice-temperature till it became homogeneous (3 hours), when it was kept aside first at 0° for 20 hours and then at room temperature (23°) for 24 hours, and finally heated to 60-65° for 1 hour. The product was cooled, diluted with water (75 c.c.) and the product taken up in ether (75 c.c.), which was washed with brine (75 c.c. × 2) and dried. After removal of the solvent, the residue was fractionated to furnish the bromide as a colorless liquid with a rather repulsive odour, b.p. 136°/3.5 mm, yield 14 g. (82.3%). An analytical sample had b.p. 138°/4 mm, n_D^{25} 1.5270, d_4^{25} 1.5240, M_D 57.28 (calc. 57.10'. (Found: C, 38.36, 38.55; H, 5.22, 5.40. $C_9H_{16}Br_2$ requires C, 38.03; H, 5.63%).

4-*Methyl*-cis-*bi*cyclo-(0 : 3 : 5)-*dec*-3-*ene*.—The *bis*-Grignard derivative of the above dibromide (7.4 g., 0.026 *M*) was prepared with magnesium (1.264 g., 0.052 g. atom) and ether (60 c.c. + 30 c.c.) in the usual manner. The reaction was generally started by adding a trace of iodine and warming, and usually took about 6-10 hours for the disappearance of magnesium; in a few cases the mixture had to be refluxed for 24 hours for the reaction to be completed. The product was next diluted with 100 c.c. of ether.

To the flask, containing the above Grignard solution, a high dilution apparatus was attached, and to the refluxing solution ethyl acetate (0.88 g., 0.01 *M*) in 100 c.c. of ether was introduced during 14 hours. After the addition, the reaction mixture

* All m.p.s are uncorrected.

was refluxed for another hour and then the ether (*ca.* 200 c.c.) was distilled off. The residue was treated with HCl (conc., 5 c.c. in 25 c.c. water) with ice-cooling. After the usual working up, the solvent was removed from the ether extract and the residue distilled, b.p. 90-125°/15 mm, yield 1.6 g. (the last drop of the distillate was greenish blue). This product was refluxed at 180° for 10 minutes with 1 g. of freshly fused potassium hydrogen sulphate. After cooling, the hydrocarbon was taken up in petroleum ether (5 c.c. × 4) and the solution passed through a column of silica gel (7 cm × 1.5 cm), which was washed with 40 c.c. of the same solvent. From the combined filtrates the solvent was carefully fractionated off and the residue distilled, b.p 90-92°/15 mm, n_D^{26} 1.4855, yield 0.6 g. (Found : C, 87.91 ; H, 12.0. $C_{11}H_{18}$ requires C, 88.0 ; H, 12.0%).

The hydrocarbon developed an orange colour in a chloroform solution of tetranitromethane. With bromine-acetic acid (Sabetay and Sabetay, *Compt. rend.*, 1934, **199**, 313) a purple coloration, changing to violet, was observed. With the Ehrlich-Müller reagent (Müller, *J. prakt. Chem.*, 1938, **151**, 233 ; 1939, **153**, 77 ; 1940, **156**, 179) a greenish blue colour was observed after several hours.

6-*Methylazulene*.—A mixture of the above hydrocarbon (280 mg.) and powdered sulphur (220 mg.) was heated at 220° for an hour under slight suction (400 mm). The product was directly distilled off at 10 mm and the deep violet distillate was taken up in 2 c.c. of petroleum ether and chromatographed over basic alumina (I, 12 cm × 1.6 cm). The washings with the solvent (50 + 25 c.c.) were colorless and were discarded ; the column was next washed with ether (20 c.c.), when the violet band was eluted out. Removal of the solvent from the violet eluates yielded 41 mg. of a deep violet liquid, which partly crystallised out. This was treated with 30 mg. of trinitrobenzene in 1 c.c. of alcohol to afford 25 mg. of the *trinitrobenzene complex*, m.p. 136-37°, which after one recrystallisation from alcohol was obtained as dark brown needles with a coppery hue, m.p. 139 40°. A small sample (10 mg.) of the product was decomposed by passage of its hexane solution through a small column of alumina to furnish 6-methylazulene as violet crystals, m.p. 82-83° (Sôrm and Fajkos, *loc. cit.*, report : azulene m.p. 83° ; trinitrobebzene complex, m.p. 141°).

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Received June 17, 1959.

[Jour. Indian Chem. Soc., Vo. 36, No. 10, 1959]

INFLUENCE OF ULTRASONIC WAVES ON ODEN'S SULPHUR SOL

By Satya Prakash and Alakh Dhari Pandey

The influence of ultrasonic waves (1 Mc/s, 225 watts electrical input to the transducer) on Oden's sulphur sol, prepared by the action of H_2SO_4 (conc.) on sodium thiosulphate, has been described. On exposure to these waves, the sol becomes unstable, exhibiting stagewise coagulation; the conductivity of the sol increases with time whereas *p*H decreases on exposure. The aged sol shows the effect of ultrasonic waves more prominently. The results have been recorded at three dilutions.

In previous publications, Prakash and Ghosh (*Kolloid Z.*, 1957, **151**, 72; 1958, **158**, 33) made a detailed study of the influence of the ultrasonic waves on the stability of a number of sols like ceric hydroxide, antimony sulphide, arsenious sulphide, vanadium pentoxide, stannic hydroxide, aluminium hydroxide, uranium ferrocyanide and Prussian blue. The results obtained on Oden's sulphur sol are recorded in the present communication.

Experimental

The sol was prepared by the action of H_2SO_4 (conc.) on $3N$ sodium thiosulphate solution in cold at 20°. The impure dispersion was coagulated with N-NaCl solution and repeptised repeatedly to remove the excess of sulphuric acid. The peptised sol was left for dialysis in a parchment bag for ten days for further purification, when a clear, yellow, opalescent sol, containing 1.284 g. of sulphur per litre, was obtained.

As described by Prakash and Ghosh (*loc.cit.*), the sols were taken in a Jena glass container and maintained in a bath at a constant temperature (25°). The ultrasonic waves were passed through the sols for various periods of time, extending to about 3 to 5 hours from Mullard's high frequency ultrasonic generator, working at 225 watts, and barium titanate transducer, furnishing a frequency of 1 Mc/s. The reactions were carried out in one and-the same reaction vessel, placed at a fixed distance from the surface of the crystal. The relative positions of the transducer and the reaction vessel were so adjusted as to furnish a good fountain, invariably accompanied with a dense fog. The volume of the sol introduced in the vessel was 30 c.c. The temperature was maintained at 25°. A small quantity of the sol was taken out from time to time for the determination of *p*H and conductivity. Glass electrodes were used for the measurement of H^+-ion concentrations.

The sol was exposed for about 4 hours at intervals of 30 minutes; the changes in conductivity and H^+-ion concentration were noted by taking small portions of the sol out of the reaction vessel. The sols were studied at different dilutions (A, A/2 and A/3 in which the original sol was A). In the second set, this effect was studied by repeating the experiments with the sol allowed to age for one month. The results are recorded in Table I (*a*, *b* and *c*).

TABLE I

Temp. = 30°.

Exposure (in mins.)	(a) With sol A. Fresh sol. Sp. condy. × 10^4. (Ohm^{-1} cm^{-1})	(a) Fresh sol. *p*H.	(a) Aged 1 month. Sp. condy. × 10^4.	(a) Aged 1 month. *p*H.	(b). With sol A/2. Fresh sol. Sp. condy. × 10^4.	(b) Fresh sol. *p*H.	(b) Aged 1 month. Sp. condy. × 10^4.	(b) Aged 1 month. *p*H.	(c). With sol A/3. Fresh sol. Sp.condy. × 10^4.	(c) Fresh sol. *p*H.	(c) Aged 1 month. Sp. condy. × 10^4.	(c) Aged 1 month. *p*H.
0	4.5975	3 40	4.2246	3.45	2.5145	3.60	2.0412	3.65	1.7732	3.65	1.5654	3.65
30	5.1185	3.35	5.5628	3.32	3.2135	3.50	3.1146	3.55	2.6925	3.55	2.9852	3.54
60	5.7326	3.25	6.6452	3.15	4.5321	3 42	4.8405	3.35	3 4528	3.45	3.9956	3.48
90	6.4522	3.10	7.4583	3.02	5 4562	3.32	5.7282	3.22	4.9456	3.32	5.0844	3.30
120	7.4380	3.05	8.6842	2.90	6.2546	3.15	6.4365	3 00	5.4526	3.24	5.8856	3.20
150	8.2756	3.00	9 0252	2.82	7.0414	3.05	7.2824	2.90	6 5428	3.12	6.9352	3.10
180	9.1434	2.90	10.1581	2.78	7.6498	2.90	8.0014	2.85	7.4825	3.00	7.8456	2.95
210	10.3528	2.82	10.6427	2.70	8.2535	2.85	9.2342	2.78	7 9535	2.90	8.3585	2.90
240	10.6485	2.75	11.5854	2.65	9.0567	2.80	10.0524	2.70	8.7420	2.85	9.2588	2.80

N. B. Sp. conductivity in ohm^{-1} cm^{-1}.

DISCUSSION

From the results recorded in Table I (*a*, *b* and *c*) it is clear that the specific conductivity continuously increases on exposing the sol to ultrasonic waves, whereas the *p*H value shows a continuous decrease. This may partly be due to the liberation of polythionic acids.

The role of pentathionic acid in the case of sulphur sols is peculiar. The acid is produced in appreciable amounts in accord with the equation (Chancel and Diacon, *Compt. rend.*, 1863, **56**, 710 ; Debus, *J. Chem. Soc.*, 1888, **53**, 278) :

$$5H_2S_2O_3 \rightarrow 2H_2S_5O_6 + 3H_2O$$

and is occluded in the colloidal micelles. These micelles are broken up under the action of ultrasonic waves, and the pentathionic acid, so liberated, goes to increase the hydrogen-ion concentration, as well as the conductivity of the sol. This influence appears to be more marked in the sol aged to about one month. The changes in *p*H are also partly due to the formation of hydrogen peroxide from the dissolved oxygen and water.

It is a well-known fact that when ultrasonic waves are passed through a liquid, small bubbles with high cavitation energy are formed. These bubbles rupture with the liberation of this energy, which appears to be responsible for various types of changes, e.g., breaking up of loose chemical bonds, liberation of adsorbed ions, rupture of micellar structures and the development of local high temperatures and pressures. We have

tried to maintain a constant temperature of the bath as a whole, but it is impossible to control the momentary localised temperature effects which in certain cases and at certain points are considerable.

TABLE II

Temp. = 25°.

Exposure (mins.) ...	60	120	180	240	300
S present in 30 c.c. of the sol* (in g.)	0.010	0.012	0.016	0.023	0.024

* With sol A

The coagulation of Oden's sulphur sol are peculiar and stepwise, the largest particles precipitating first, followed by the smaller ones in order of decreasing size. The sol in this respect may be regarded as polydispersed one. The precipitated sulphur during the exposure of the sol to the ultrasonic waves was filtered out and weighed as such in a sintered glass crucible from time to time. The results are recorded in Table II which show that the sol becomes unstable under the action of these waves.

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Received February 2, 1959.

[Jour. Indi Cheanm. Soc., Vol. 36, No. 10, 1959]

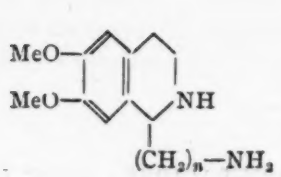
*iso*QUINOLINE DERIVATIVES AS POSSIBLE AMOEBACIDES. PART I

By T. N Ghosh, Sunil Kumar Ganguly and Bhabatosh Bhattacharya

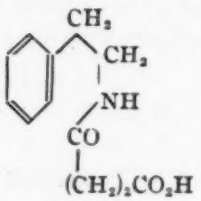
Malondi-β-phenethylamide undergoes the Bischler-Napieralski cyclisation to yield 1:1′-methylene-*bis*-3:4-dihydro*iso*quinoline. *N*-α-Methyl-β-phenethylcyanoacetamide similarly cyclises to yield 1-cyanomethyl-3-methyl-3:4-dihydro*iso*quinoline, which furnishes (X) on reduction.

Emetine is a specific drug for the treatment of acute stages of amoebic dysentery. It also exerts beneficial effect in amoebic hepatitis. Nevertheless, it cannot be classed as an ideal drug because of its several unpleasant side effects, its narrow margin of safety and cumulative toxic action on the myocardium. Further, the mode of action of emetine has not been clearly understood. It is surmised that the drug undergoes degradation in the system and the specific action might be attributed to one or more of such degradation products. The hypothetical cleavage of the emetine molecule can, depending upon the lines of cleavage, give rise to several types of bases, some of which have been synthesised and evaluated (Pyman, *Chem. & Ind.*, 1937, **56**, 789; Goodson *et al.*, *Brit. J. Pharmacol.*, 1948, **3**, 49; Sugasawa, *J. Pharm. Soc. Japan*, 1949, **69**, 8; Hall *et al.*, *J. Chem. Soc.*, 1950, 1842; Osbond, *ibid.*, 1951, 3464; 1952, 4785; Mahboob and Dhar, *J. Sci. Ind. Res.*, 1955, **14B**, 1; Kachru and Pathak, this *Journal*, 1957, **34**, 611, 768). Amongst these bases, the structures of which have not materially been affected by the correction of the emetine structural formula (Robinson, *Nature*, 1948, **162**, 524; Battersby and Openshaw, *J. Chem. Soc.*, 1949, *S*59, *S*67, 3207), only a few compounds, specially *bis*-diamylaminodecane (Pyman, *loc. cit.*), showed promise *in vitro*, but none has so far proved *in vivo* as effactive as emetine.

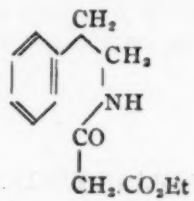
Hypothetical cleavage of the emetine molecule along other visualised lines may give rise to the pattern (I), and it has been considered to be of interest to synthesise *iso*quinolines related to (I) for evaluation against amoebiasis. As a preliminary approach to the problem, β-phenethylsuccinamic acid (II) has been prepared by condensation of β-phenethylamine with succinic anhydride. It was planned to convert (II) into the corresponding amide, which could then be subjected to the Bischler-Napieralski cyclisation. However, passing dry ammonia into (II) in the liquid stage at 140-45° or at 180-85° or treatment of (II) with thionyl chloride with the object of obtaining the corresponding acid chloride or even heating (II) at 180-85° alone, invariably gave rise to *N*-β-phenethylsuccinimide (Child and Pyman, *J. Chem. Soc.*, 1929, 2010). Further, the attempted Bischler-Napieralski cyclisation of (II) with phosphorus pentoxide in toluene led to its breakdown, the only product isolable being β-phenethylamine.



(I)

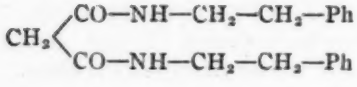


(II)

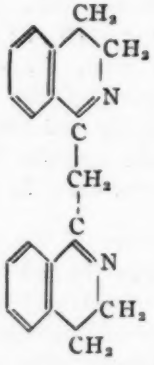


(III)

Battersby *et al.* (*J. Chem. Soc.*, 1953, 2463) obtained solely ethyl *N*-3 : 4-dimethoxyphenethylmalonamate by heating 3 : 4-dimethoxyphenethylamine at 125° with an excess of ethyl malonate. With the object of obtaining (III), related to (II), β-phenethylamine has now been similarly heated at 125-30° with an excess of ethyl malonate to furnish, however, malondi-β-phenethylamide (IV) (Child and Pyman, *loc. cit.*) as the major product, mixed with a small quantity of ethyl β-phenethylmalonamate (III). The poor yield of (III) and the difficulty encountered in its separation from (IV) rendered this approach to the problem unfeasible. However, it is significant to observe that, contrary to the observation of Child and Pyman (*loc. cit.*), (IV) underwent the Bischler-Napieralski cyclisation in presence of phosphorus pentoxide in toluene to yield 1 : 1′-methylene-*bis*-3 : 4-dihydro*iso*quinoline (V), which was dehydrogenated over Pd-C to furnish 1 : 1′-methylene-*bis*-*iso*quinoline (V), characterised as dipicrate.



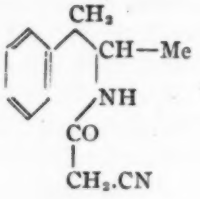
(IV)



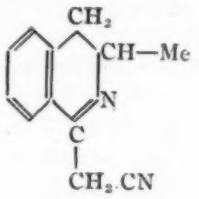
(V)

The next approach to (I) involved reacting α-methyl-β-phenethylamine with an excess of ethyl cyanoacetate at 130-40° to furnish *N*-α-methyl-β-phenethylcyanoacetamide (VII), which cyclised in presence of phosphorus pentoxide in toluene to 1-cyanomethyl-3-methyl-3 : 4-dihydro*iso*quinoline (VIII). (VIII) was dehydrogenated over Pd-C to the corresponding aromatised *iso*quinoline (IX). Reduction of (VIII)

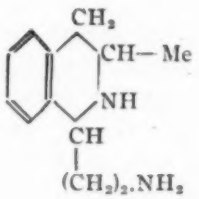
with sodium and ethanol (cf. Wegler and Frank, *Ber.*, 1937, **70**, 1279 : Allewelt and Day, *J. Org. Chem.*, 1941, **6**, 384) has furnished β-(3-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinolyl)-ethylamine (X), structurally related to (I).



(VII)



(VIII)



(X)

EXPERIMENTAL

β-Phenethylsuccinamic Acid (II).—Succinic anhydride (10 g) was added to β-phenethylamine (12.1 g.) in benzene (150 c.c.) and the mixture was heated under reflux for 4 hours. On cooling, the solid (18 g.) was filtered and crystallised from water in colorless plates, m.p. 125-26°. (Found : N, 6.47. $C_{12}H_{15}O_3N$ requires N, 6.33%).

When dry ammonia gas was passed into (II) at 140-45° or at 180-85° or when (II) was heated at 180-85° alone, a compound crystallising from ethanol in colorless prisms, m.p. 134-35°, was obtained and was identified to be *N*-β-phenethylsuccinimide (Child and Pyman, *loc. cit.*, record m.p. 133-34°). (Found : N, 7.23. Calc. for $C_{12}H_{13}O_2N$: N, 6.90%).

Condensation of β-Phenethylamine with Ethyl Malonate : Formation of Ethyl β-Phenethylmalonamate (III) *and Malon-di-β-phenethylamide* (IV).—A mixture of β-phenethylamine (11 g.) and ethyl malonate (44 g.) was heated under reflux in an oil-bath at 125-30° for 8 hours. After removal of the excess of ethyl malonate under reduced pressure, the liquid was distilled and the fraction (b.p. 140-230°/10mm) collected.

The residue gradually solidified and was extracted with hot ethanol and precipitated by addition of water. The solid (7 g.) was crystallised from water in colorless needles, m.p. 131-32°. (Found : N, 8.87. Calc. for $C_{19}H_{22}O_2N_2$: N, 9.03%). It was identified to be (IV) (Child and Pyman, *loc. cit.*, record m.p. 129-30°).

The above fraction was redistilled at 1 mm pressure. The fraction up to 110° was rejected. The fraction distilling above 110° was collected and it solidified when kept in the refrigerator for several days. It was filtered, pressed and crystallised from petroleum ether (b.p. 60-80°) in colorless needles (III, 0.65 g.), m.p. 61-62°. (Found : N, 6.18. $C_{13}H_{17}O_3N$ requires N, 5.95%).

The *anilide* was crystallised from aqueous ethanol in colorless, rectangular plates, m.p. 155-56°. (Found : N, 10.22. $C_{17}H_{18}O_2N_2$ requires N, 9.93%). When (III) was heated with hydrazine hydrate in ethanolic solution, a compound (m.p. 153°),

identified to be malondihydrazide, was obtained, evidently by the cleavage of the amide linkage (cf. Bergmann and Zervas, *J. Biol. Chem.*, 1936, **113**, 341).

1 : 1′-*Methylene*-bis-3 : 4-*dihydro*isoquinoline (V).—A mixture of the diamide (IV, 8 g.) and P_2O_5 (32 g.) in anhydrous toluene (160 c.c.) was refluxed under mechanical stirring in an oil-bath for 4 hours. The mixture was cooled in ice and treated with ice-water. The aqueous layer was separated, washed with ether, treated with charcoal and filtered. The filtrate, on basification with caustic soda, furnished a pasty solid (3.3 g.), which was purified by acid-alkali treatment and finally by extraction with warm benzene. It was crystallised from ethanol (charcoal) in fine yellow needles, m.p. 126-27° and dried *in vacuo* over P_2O_5. (Found : C, 83.48 ; H, 6.72 ; N, 10.23. $C_{19}H_{18}N_2$ requires C, 83.21 ; H, 6.57 ; N, 10.22%).

The *picrate* was crystallised from ethanol in shining yellow needles, m.p. 233-34° (decomp.). (Found : N, 14.21. $C_{19}H_{18}N_2.C_6H_3O_7N_3$ requires N, 13.92%).

1 : 1′-*Methylene*-bis-iso*quinoline* (VI).—A mixture of (V, 2.5 g.) and palladium-charcoal (10%, 0.8 g.) in tetralin (12 c.c.) was heated under reflux in an oil-bath at 240-45° in an atmosphere of CO_2. After removal of Pd—C, the liquid was extracted with HCl (dil.) and the acid solution, on basification with caustic soda, furnished a pasty mass (2 g.), the *dipicrate* of which was obtained in ethanol and recrystallised from ethanol as yellow flakes, m.p. 228-29°. (Found : N, 15.63. $C_{19}H_{14}N_2.2\,C_6H_3O_7N_3$ requires N, 15.38%).

The base (VI) was crystallised from aqueous alcohol in cream-coloured needles, m.p. 134-35°. (Found : N, 10.21. $C_{19}H_{14}N_2$ requires N, 10.37%).

N-α-*Methyl*-β-*phenethylcyanoacetamide* (VII).—A mixture of α-methyl-β-phenethylamine (13.5 g.) and ethyl cyanoacetate (34 g.) was heated in an oil-bath at 130-40° in a flask, fitted with a downward condenser, for 6 hours, during which period the ethanol formed distilled over. The residual liquid was distilled under reduced pressure to remove excess of ethyl cyanoacetate and another fraction, small in quantity, could be collected up to 140°/27-28 mm and was rejected. The residual mass (18 g.), on keeping in an evacuated desiccator, gradually solidified and the solid was crystallised from petroleum ether (b.p. 60-80°) as colorless flakes, m p. 70-71°. (Found : N, 13.97. $C_{12}H_{14}ON_2$ requires N, 13.86%).

1-*Cyanomethyl*-3-*methyl*-3 : 4-*dihydro*isoquinoline (VIII).—A mixture of (VII, 12 g.), P_2O_5 (48 g.) and anhydrous toluene (180 c.c.) was used and the method of procedure was the same as described previously. The crude base (4 g.) was crystallised from ethanol (charcoal) in yellowish needles, m.p. 93-94°. (Found : N, 14.95. $C_{12}H_{12}N_2$ requires N, 15.22%).

The *picrate* was crystallised from ethanol in greenish yellow needles, m.p. 163-64°. (Found : N, 17.14. $C_{12}H_{12}N_2.C_6H_3O_7N_3$ requires N, 16.95%).

1-*Cyanomethyl*-3-*methyl*isoquinoline (IX).—The method of dehydrogenation was the same as described previously. The base was characterised as *picrate*, crystallising from ethanol in yellow rectangular plates, m.p. 187-88°. (Found : N, 17.21. $C_{12}H_{10}N_2.C_6H_3O_7N_3$ requires N, 17.03%).

β-(3-Methyl-1:2:3:4-tetrahydroisoquinolyl)-ethylamine (X).—Sodium (6 g.) was slowly added under stirring to a solution of (VIII, 6 g.) in anhydrous ethanol (100 c.c.) and the mixture was gently heated under reflux to dissolve all the sodium. The mixture was then cooled and diluted with water (100 c.c.). The liquid was distilled off and the residue extracted with ether. From the ether solution the base was extracted with HCl (dil.) and precipitated by alkali. By addition of ether to an ethanolic solution of the base, saturated with dry HCl gas, the *dihydrochloride* was obtained as a brownish microcrystalline powder, m.p. 249-50°. (Found : N, 10.52 ; Cl, 27.54. $C_{12}H_{18}N_2.2HCl$ requires N, 10.65 ; Cl, 26. 96%).

The authors are indebted to Dr. U. P. Basu, Director of the Institute, for his interest in this investigation. One of the authors (S.K.G.) is grateful to the Ministry of Scientific Research & Cultural Affairs, Government of India, for the award of a scholarship.

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Received June 24, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

A STUDY ON THE REACTION BETWEEN MILLON'S BASE AND ALKALI METAL SALT SOLUTIONS

By Nripendra Nath Ghosh

The reaction between Millon's base and aqueous solutions of alkali metal salts, such as, chloride, bromide, iodide, nitrate, sulphate, phosphate, etc., has been studied. In all the cases the removal of the anion with Millon's base is not quantitative. The results may be represented according to easy extractibility of the anions with Millon's base in the following order : Cl^-, Br^-, $I^- > HPO_4^{2-} > SO_4^{2-} > NO_3^- > ClO_4^-$.

Quantitative estimation of the alkali metals with Millon's base as the reagent is possible, when these are present as chlorides, bromides or iodides.

It is well known that anions from an aqueous solution of a metal salt can be extracted with Millon's base and the corresponding hydroxide of the metal is formed (Biltz and Biltz, "Laboratory Method of Inorganic Chemistry," 1st. ed., 1909, John Wiley & Sons, New York, p. 162). In order to make a quantitative study of the reaction of Millon's base on the alkali metal salt solution, the present work was undertaken. A preliminary note on the subject was published previously (Ghosh, *Science & Culture*, 1955, **20**, 165).

If the extraction of anion from the alkali metal salt solution with Millon's base be complete, the alkali metal, which would be present as hydroxide, could be estimated by acidimetry. Alkali metal salts as chloride, bromide, iodide, nitrate sulphate, phosphate, etc. have been systematically treated with Millon's base and the alkali liberated has been estimated quantitatively. It has been found that only in the cases of chloride, bromide and iodide, the alkali metal hydroxide formation is quantitative, and in other cases the complete removal of anion has not been possible. The results may be arranged in the following manner according to easy extractibility of the anion with Millon's base: Cl^-, Br^-, $I^- > HPO_4^{2-} > SO_4^{2-} > NO_3^- > ClO_4^-$. It has also been found qualitatively that the complete removal of vanadate ion could not be made by treating an alkali vanadate solution with Millon's base.

Therefore the alkali metals can be estimated using Million's base as the reagent, if these are present as chlorides, bromides or iodides. The use of Millon's base can also be made as an anion exchanger. Like cation-exchanger (Kunin and Myers, "Ion Exchange

Resins", 3rd. Printing, John Wiley & Sons, New York, 1952, p. 91) it has been found that the fraction of many alkali metal salts, which have not been converted into alkali, increases as the concentation of the salt increases. Further work is in progress.

EXPERIMENTAL

Reagents used were of A. R. quality. Millon's base was prepared by following the method described by Biltz and Biltz (*loc. cit.*). All solutions were made with double-distilled water.

Standard solutions of alkali metal salts were prepared, strengths being approximately 0.2 *N* to 0.05 *N*. The general procedure of the treatment with Millon's base was as follows. Each standard solution was taken in aliquots of 5, 10 15, 20, 25 c.c. etc. and the volume was made up to 50 c.c. after adding Millon's base (~ 1g. to 1.5 g.). The solution was then allowed to stand with occasional shaking till the suspended particles had settled down. It was then filtered and neglecting the first few c.c., 25 c.c. of the filtrate was titrated against standard H_2SO_4. The total alkali liberated was then calculated. Results obtained against chloride, bromide and iodide are recorded in Table I.

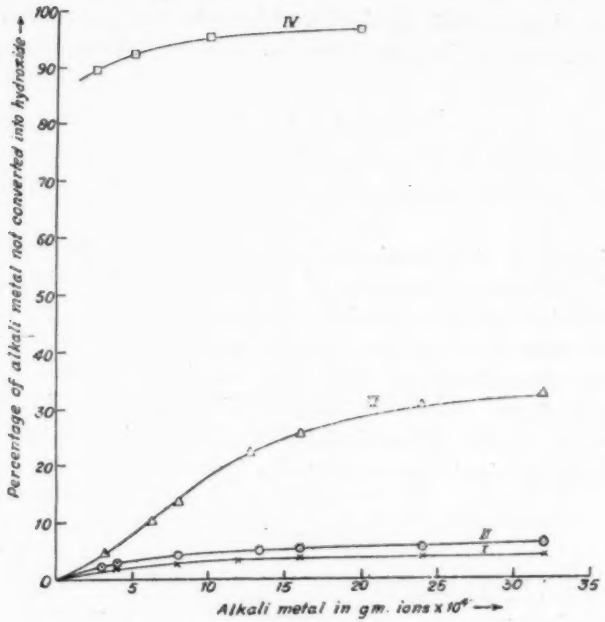
TABLE I

Halide soln. taken.	0.1048 *N*-H_2SO_4 reqd. for 25 c.c. of the filtrate.	K^+ (g.ion × 10^4) Present	Found.	% Error.
		A. 0.08 *M*-KCl soln.		
5 c.c.	1.90 c.c.	4.0	3.98	−0.50
10	3.80	8.0	7.97	−0.37
15	5.75	12.0	12.05	+0.42
20	7.65	16.0	16.04	+0.25
25	9.55	20.0	20.02	+0.10
30	11.45	24.0	24.00	±0.00
		B. 0.095 *M*-KBr soln.		
5	2.25	4.75	4.72	−0.63
10	4.55	9.50	9.54	+0.42
15	6.80	14.25	14.25	±0.00
20	9.05	19.00	18.97	−0.16
		C. 0.067 *M*-KI soln.		
10	3.20	6.70	6.71	+0.15
15	4.80	10.05	10.06	+0.09
20	6.40	13.40	13.42	+0.15
25	8.00	16.75	16.77	+0.12

The following solutions were also similarly treated: (*a*) sodium sulphate, 0.2*N*; (*b*) potassium nitrate, 0.16 *N*; (*c*) disodium hydrogen phosphate, 0.2 *N*; (*d*) potassium sulphate, 0.2 *N*; (*e*) potassium perchlorate, 0.05 *N*.

The results are represented graphically in Fig. 1.

FIG. I.



I -Alkali metal phosphate HPO_4^{2-}
II - ,, ,, sulphate SO_4^{2-}
III- ,, ,, nitrate NO_3^-
IV- ,, ,, perchlorate ClO_4^-

The author expresses his sincere thanks to Prof. P. B. Sarkar for providing laboratory facilities.

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Received June 24, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

KINETICS OF ANION-EXCHANGE REACTION IN ETHANOL AS SOLVENT. EXCHANGE OF Cl^- ION ON AMBERLITE IR-4B

By R. P. Shukla and R. P. Bhatnagar

Kinetics of the anion-exchange reactions on Amberlite IR-4B in non-aqueous solvent (eg., ethanol) has been studied. The effects of addition of water to the system and of stirring have also been investigated.

In an earlier communication (this *Journal*, 1955, **32**, 39) it has been pointed out that cation-exchange reactions in solvents other than water (viz., ethanol and acetone) do not obey ordinary first or second order reaction mechanism. These, on the other hand, follow the reversible second order rate equation. The present work incorporates similar studies for anion-exchange reaction in a solvent other than water. The work on the kinetics of anion-exchange reaction by others is comparatively little. Though some workers (Nachod and Wood, *J. Amer. Chem. Soc.*, 1944, **66**, 1380 ; Samuelson, *Svensk. Papperstidn.*, 1943, **46**, 583) have tried anion-exchange kinetics in aqueous solution, only a few (Chance *et al.*, *Chem. Abs.*, 1952, Sept.) have tried it in non-aqueous solvents. Even in the cited work, the resins used were water-wet. Hence, the attempt cannot be regarded to be strictly in non-aqueous systems. The present work therefore has been carried out in a purely non-aqueous system. The effect of addition of water to such a system and the effect of stirring have been studied.

Experimental

The chloride solutions for exchange purposes were prepared by dissolving anhydrous lithium chloride (A.R.) in anhydrous ethanol. The use of potassium chloride or sodium chloride was not possible due to their insolubility in absolute alcohol. Every possible care was taken to keep the solutions, thus prepared, out of contact with atmospheric moisture. The strengths of the prepared solutions, with respect to chloride ion, were confirmed by taking aliquots (10 c.c.) in a beaker, precipitating the chloride ion with a known excess of a standard silver nitrate solution and then titrating the excess of silver nitrate in the solution by Volhard's method.

For kinetic studies always 100 c.c. of the chloride solution in ethanol was taken in the reaction vessel (500 c.c. capacity, three-necked, round-bottomed flask) provided with the stirring arrangement (Mechanical stirrer of M/s Baird and Tatlock Ltd., London). It was stoppered immediately The stirrer was started and then 4 g. of the vacuum-dried anion-exchange resin, Amberlite IR-4B in the hydroxyl form, was added by removing one of the stoppers of the three-necked flask for a moment. At suitable time intervals aliquots (5 c.c.) of the solution from the reaction vessel were withdrawn quickly and the chloride was estimated by Volhard's method (indirect estimation of halides). The concentration of chloride ion at equilibrium (t = infinity) was found out by titrating an aliquot from the solution after seven days. The reactions were carried out under thermostatic conditions at 30°. The results have been summarised in Table I.

The effect of stirring was studied by performing kinetic studies first in a solution by stirring the solution in the reaction vessel intermittently with hand and then by studying the kinetics in a mechanically stirred solution (~300 r. p m.).

TABLE I

Resin: Amberlite IR-4B (4 g.). Temp. = 30°.

Sr. No.	Stirring.	Solvent.	[LiCl] × $10^{-3}M$.	Average $K \times 10^3$.
1.	Hand	EtOH (anhyd.), 100 c.c.	20.876	0.22565
2.	Mechanical	Do	20.876	0.69679
3.	Mechanical	Do	10.000	0 88809
4.	Mechanical	Do + 20 c.c water	10.000	3.19014
5.	Mechanical	Do + 60 c.c. ,,	10.000	13.15700
6.	Mechanical	Do + 80 c.c. ,,	10 000	13.57020
7.	Mechanical	Do + 160 c.c. ,,	10.000	30.98300

N.B. Values of K are found out with respect to $\log_{10}$ values, and are average values The derivation in particular sets of readings can be seen from Fig. 1.

Effect of Addition of Water.—It was studied by following the rate of reaction in different solutions with varying volumes of double-distilled water in them. These were also carried out at 30° and with mechanical stirring, as detailed above (Table I, readings 4, 5, 6 and 7).

The effect of variation of temperature on rate constant in preliminary studies at two different temperatures (20° and 30°) pointed out that it had no appreciable effect on K. High temperatures were not possible with an organic solvent of low b.p. (as ethanol). Moreover, the independence of K with temperature in the case of aqueous exchange kinetics has been shown by Nachod and Wood (*loc. cit.*).

DISCUSSION

The above studies, performed with Cl^- ion as the anion in ethanol (anhydrous) solution on Amberlite IR-4B in hydroxyl from, can be considered to be following the exchange reaction as

$$R.OH + Cl^- \rightleftharpoons R.Cl + OH^- \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

The OH^- ion formed as a result of the forward reaction in eq. (1) starts the backward reaction simultaneously and, hence, the reaction involved is a reversible one.

The present authors have shown that the cation-exchange reaction (*loc. cit.*) follows a similar mechanism and have come to the conclusion that the equation that satisfies the condition for such a reversible process is

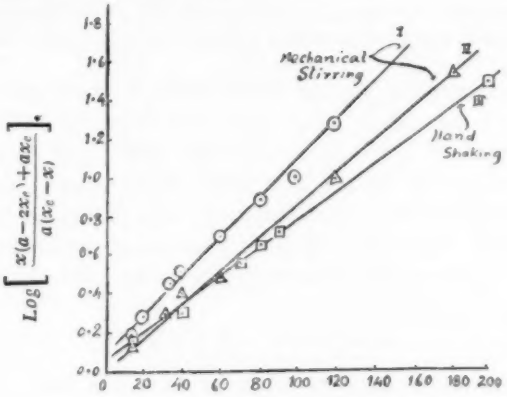
$$\log \frac{x(a-2x_e)+ax_e}{a(x_e-x)} = K.\frac{2a(a-x_e)}{x_e}.t \quad \ldots \quad \ldots \quad (2)$$

where x is the change in concentration at time t, a is the initial concentration (at $t = 0$), x_e is the change in concentration at t = infinity or when equilibrium has been reached and K is the velocity constant. As the equation (1) is also a reversible one, it can be shown here too that equation (2) should be applied in the case of anion-

exchange kinetics in non-aqueous media. In equation (2) the term $2a(a-x_0)/x_0$ is constant (k'), and it can be put in the form:

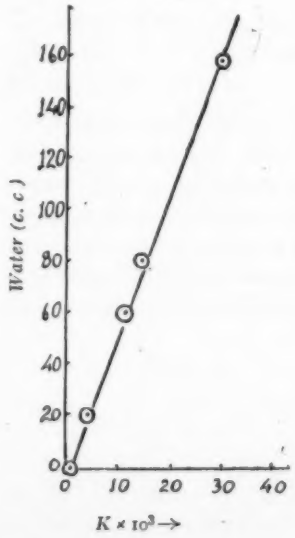
$$\log \frac{x(a-2x_0)+ax_0}{a(x_0-x)} = Kk't \qquad \ldots \qquad \ldots \quad (3)$$

Thus, if the suggested mechanism is correct, a plot of the term on the left hand side of equation (3) against time should provide a straight line in each case. We have plotted this in Fig. 1 and have obtained straight lines, showing the validity of this equation of reversible second order.



The same equation has been used to find out the values for K in partly aqueous solution (*i.e.* after addition of known volumes of water to the reaction mixture). The reasonable consistency of K values confirm the fact that the same reversible second order reaction mechanism is followed in the partly aqueous media also. We have also plotted in Fig. 2 the variation of K with the increase of water (in c.c.) in the non-aqueous solution. The plot, which is a straight line, indicates progressive rise in the velocity constant. It follows therefore that by the addition of water to the non-aqueous systems, the anion-exchange reaction becomes faster and faster and tries to become almost instantaneous, when water content is too large.

FIG. 2



The effect of stirring is clear (from readings 1 and 2 in Table I). Stirring makes the rate faster. Moreover, it may be emphasised here that the exchange reaction is to be supposed as a homogeneous ionic replacement (as is concluded by Monger and Wassermann, Disc. Faraday Soc., 1949, No. 7, p. 118) and not a diffusion step (as is given by Boyd *et al.*, *J. Amer. Chem. Soc.*,

1947, **69**, 2836). The stirring at a moderately high speed in aqueous solvents of low boiling points causes change in the initial concentrations to a great extent due to splashing of the liquid on to the sides of the reaction vessel and also due to slow volatilisation of the solvent itself. The moderately high speed of stirring ensures a thorough mixing of the two phases, which is important to cause the phenomenon in a manner similar to a homogeneous ionic replacement, represented by the simple equation (1).

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Received April 30, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

ELECTRICAL CONDUCTIVITY OF STANNIC OXIDE SOL

By R. S. Parikh, M. J. Patani and A. M. Trivedi

In well-dialysed stannic oxide sols, prepared by peptising precipitated stannic hydroxide with ammonia, when allowed to age, the specific conductivity increases due to the desorption of ammonium stannate, the stabilising electrolyte. The sol behaves as a typical colloidal electrolyte, the equivalent conductivity of the micelles first decreasing and then increasing on further dilution.

The electrical conductivity of stannic oxide sols has been studied by a number of workers including Ghosh (*J. Chem. Soc.*, 1929, 2290, 2298) and Dhar and Vardhanam (this *Journal*, 1932, **13**, 602). Jha and Ghosh (*ibid.*, 1945, **22**, 271) studied the effect of ageing on the conductivity of stannic oxide sols diluted to different extents. In the present investigation, negatively charged stannic oxide sols have been studied by measuring the change in conductivity on ageing as well as on dilution. Results obtained have been discussed to elucidate the nature of the stabilising electrolyte.

Experimental

Several methods were employed by different investigators to prepare the stannic oxide sols (Graham, *Phil. Trans.*, 1861, **151**, 213 ; Schneider, *Z. anorg. Chem.*, 1894, **5**, 82 ; Zsigmondy, *Annalen*, 1896, **301**, 361 ; Ghosh, *loc. cit.*; Dhar and Vardhanam, *loc. cit.* ; Jha and Ghosh, *loc.cit.*; Aditya, this *Journal*, 1952, **29**, 296). In the present investigation, negatively charged, concentrated stannic oxide sols were prepared by peptising well-washed stannic hydroxide precipitate with the minimum quantity of liquor ammonia. The excess of ammonia was removed on heating the sol, which was further purified by subjecting it to continuous hot dialysis (Neidle and Barab, *J. Amer. Chem. Soc.*, 1916, **38**, 1962 ; 1917, **39**, 71).

Stannic oxide content was determined by evaporating an aliquot portion of the sol to complete dryness whereby the ammonium salts escaped to the atmosphere. An aliquot portion of the sol was coagulated, filtered and washed with Na_2SO_4 solution and the ammonium ion estimated by treating the filtrate with standard sodium hydroxide and then titrating the excess of the latter with a standard HCl solution. Chloride was found to be absent in all the sols under investigation. Several samples of the sol were studied. Table I records composition of the sols G and H.

Table I

Sol.	SnO_2.	NH_4^+ ion.	Purity.
G	29.15 g./litre	0.1872 g./litre	156
H	48.12	0.5040	95

Change in Conductivity on Ageing.—The conductivity of the sol G, diluted to different extents, was measured over a number of days. Double-distilled water

(sp. condy. = 2.0×10^{-6} mhos) was employed for dilutions, its conductivity being neglected in calculating the conductivity of the sols. The conductivity of the sols was measured at $35° \pm 0.1°$ as before (Trivedi *et al.*, *Proc. Ind. Acad. Sci.*, 1952, **36**, 530). Table II represents the change in sp. conductivity on ageing in the case of sol G.

TABLE II

Sol G.

No. of days.	Specific conductivity × 10^4. 100%.	50%.	25%.	12.5%.
0	2.948 mho	1.367 mho	0.6728 mho	0.3771 mho
1	2.918	1.420	0 7214	0.4091
2	2.953	1.429	0.7565	0.4228
4	2.942	1.446	0.7770	0.4637
8	2.968	1.468	*...	0.5045
18	2.970	1.488	...	0.5614
22	2.975	1.498	...	0.5971
35	2.986	1.514	...	0.6253
47	3.025	1.562	...	0.6479
78	3.062	1.592	...	0.7038

* Sample lost accidentaly.

Change in Conductivity on Dilution.—Sol H after proper dilution was used for the measurement of conductivity. Table III represents the specific and the equivalent conductivities of the micelles at different dilutions. The cell constant of the cell employed was 1.776.

TABLE III

Sol : H

Conc.	Sp. condy. × 10^4.	Eq. condy.	Conc.	Sp. condy. × 10^4.	Eq. condy.
48.12 g./litre	6.880 mho	24.57	24.06 g./litre	3.205 mho	22 81
43.30	6.129	24.32	19.25	2.528	22.57
38.46	5.378	24.01	14.44	1.913	22.77
33.68	4.632	23.63	9.62	1.265	22.59
28.87	3.905	23.24	4.81	0.7465	26.65

DISCUSSION

Effect of Ageing.—Table II records the change in sp. conductivity on ageing in the case of sol G. The results in general are of the same nature as obtained by Jha and Ghosh (*loc.cit.*). These workers explain the change in conductivity on ageing as follows:

"A sol of stannic oxide, peptised by ammonia, is a complex aggregate of ammonium stannate....Ammonium stannate in solution, on ageing, undergoes hydrolysis in solution, forming colloidal stannic hydroxide. Such a chemical change in solution would necessarily result in a decrease in electrical conductivity of stannic hydroxide sol. The decrease in conductivity of concentrated sol of stannic hydroxide has been noted up to a certain minimum, after which there is an increase. As it is the natural tendency of all colloidal particles to give out adsorbed electrolyles with age, this explains the

increase noted in the later part of the observation. In the case of diluted sols the hydrolysis is very nearly complete, and the equilibrium between adosorbed and free electrolytic ions is gradually shifted due to an excess of water being present. That is why, there is a continuous increase in the electrical conductivity of dilute sols of stannic hydroxide, the phenomenon being most prominent with very dilute sols".

The above explanation appears to be rather vague, specially that dealing with the increase in conductivity of diluted sols. Since purified stannic hydroxide is peptised with ammonia, it may be stablised by OH^- or SnO_3^{2-} with NH_4^+ as the gegenion. In other words, stabilising electrolyte may be either ammonium hydroxide or ammonium stannate. The increase in conductivity on ageing of dilute sols cannot be explained if ammonium hydroxide is the stabilising electrolyte, as it is a weak electrolyte. Hence, we may assume that ammonium stannate is the stabilising electrolyte and the increase in conductivity is due to its coming out in the intermicellar liquid. In the case of concentrated sols, on the other hand, there is a tendency of decrease in conductivity on ageing, as ageing results in changing the stabilising electrolyte from ammonium stannate to ammonium hydroxide, as suggested by Jha and Ghosh (*loc.cit.*). Thus, there are two tendencies in the colloidal system : (*a*) change in the nature of the stabilising electrolyte which results in the decrease in conductivity and (*b*) a more powerful tendency of the stabilising electrolyte, coming out in the intermicellar liquid, resulting in the increase in conductivity.

In this connection it will be interesting to examine the hydrolysis of ammonium stannate under the conditions of experiments (concentration = 0.02 g.equiv./litre). There appears to be no reference in the literature of the properties of ammonium stannate. However, taking sodium stannate to be hydrolysed to an extent of 2.7% in the normal solution (Mellor, "A Comprehensive Treatise in Inorganic and Theoretical Chemistry", 1947, Vol. VII, p. 416 ; vide Zocher, *Z. anorg. Chem.*, 1920, **112**, 1) the hydrolytic constant can be calculated ($K_h = 8.095 \times 10^{-5}$). Taking ionic product of water, $K_w = 10^{-14}$, the dissociation constant of stannic acid (K_a) can be calculated ($K_a = 1.2 \times 10^{-10}$ approx.). From these two values, it is possible to calculate K_h and the degree of hydrolysis of ammonium stannate (conc. = 0.02 g.equiv./litre). The values come out to be 4.5 and almost 100% respectively. Hence, it appears difficult to explain the increase in conductivity due to desorption of ammonium stannate. The only plausible explanation appears to be the assumption that the hydrolysis of ammonium stannate is inhibited, as it is adsorbed on the colloidal particles. Thus, there would be the following states of equilibria :-

$$\underset{\text{(adsorbed)}}{(NH_4)_2SnO_3} \rightleftharpoons \underset{\text{(free)}}{(NH_4)_2SnO_3} \rightleftharpoons 2NH_4^+ + SnO_3^{2-}$$

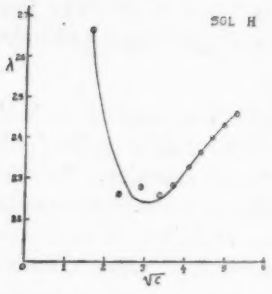
$$\downarrow H_2O$$

$$2NH_4OH + H_2SnO_3$$

Hence, ammonium stannate may not be completely hydrolysed in the presence of adsorbed ammonium stannate. If the hydrolysis takes place completely, the equilibrium will be shifted on the right hand side and the sol should become immediately unstable on dilution.

Effect of Dilution.—If we compare the variation of equivalent conductivity of the micelles on dilution with the variation of the conductivity of the free electrolyte on similar dilutions, it is found that unlike the free electrolyte, the eq. conductivity of the micelles first decreases and then increases on further dilution. The behaviour of stannic oxide sol is in harmony with the sulphur sol (Bolam and Trivedi, *Trans. Faraday Soc.*, 1943, **39**, 247), the iron oxide sol (*loc.cit.*), the chromium oxide sol (Trivedi *et al.*, this *Journal*, 1956, **33**, 115) and the aluminium oxide sol Trivedi and Buch, *ibid.*, 1957, **34**, 337). Hence, like soap solutions, such a system may be classified amongst colloidal electrolytes (McBain, *J. Amer. Chem. Soc.*, 1928, **50**, 1636).

FIG. 1



Effect of Purity on Conductivity.—Table IV records the values of specific conductivity determined graphically of the sols H and G at definite concentrations. Specific conductivity has been observed to decrease with purity. This is supported by Dhar and Vardhanam (*loc.cit.*) in the case of stannic oxide sol and by Chakravati and Dhar (*J. Phys. Chem.*, 1926, **30**, 1646) and Trivedi *et al.* (*loc. cit.*, 1956) in other colloidal systems.

TABLE IV

Conc. of the sol (SnO_2 in g./litre).	Sp. conductivity × 10^4. Sol H.	Sol G.
10.0	1.30 mho	0.95 mho
15.0	2.00	1 45
20.0	2.65	2.00
25.0	3.35	2.50
30.0	4.10	3 05

Thanks of the authors are due to the Ahmedabad Education Society for a generous grant towards chemicals and apparatus and the Gujarat University for a research grant.

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Received March 5, 1959.

[Jour Indian Chem. Soc., Vol. 36, No. 10, 1959]

FRIES REARRANGEMENT OF CINNAMATES OF MONOHYDRIC PHENOLS

By C. M. Christian and G. C. Amin*

The Fries rearrangements of phenyl cinnamate, 2-methyl-, 3-methyl-, 4-chloro-5-methyl- and 4-benzoylphenyl cinnamates afford 4- or 2-cinnamoyl phenolic compounds or chalkones, identified by direct comparison with authentic samples. 4-Methyl-, 2-chloro-, 2:4-dichloro-, 2:4 libromo-phenyl and 1-naphthyl cinnamates yield only uncrystallisable pasty masses on attempted rearrangement under usual conditions.

Though the Fries rearrangement has been extensively studied with a view to preparing specific compounds (Blatt, *Chem. Rev.*, 1940, **27**, 413 ; "Organic Reactions", John Wiley & Sons Inc., New York, Vol. I, 1942, Ch. 11, p. 342) and to studying its mechanism (Baltzly *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 2522 ; Cullinane and Edwards, *J. Chem. Soc.*, 1958, 2926 et seq), the instances of its application to the phenolic esters of the unsaturated acids are relatively few (Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56 ; Sen and Misra, this *Journal*, 1948, **25**, 393). In the present communication, the Fries isomerisation of the cinnamoyl esters of the monohydric phenolic derivatives, involving cinnamic acid as aromatic unsaturated acid, has been described.

Phenyl cinnamate (I: R=H) under the conditions of the Fries migration yielded a product which had been assigned the constitution 4-cinnamoylphenol (II: R=H) as it was found on comparison to be identical with an authentic specimen prepared by condensing 4-hydroxyacetophenone (III: R=H) with benzaldehyde in presence of potassium hydroxide (Kostanecki and Tambor, *Ber.*, 1899, **32** 1924). It was further characterised by preparing its functional derivatives.

Similarly, the cinnamates of 2-methyl- and 3-methyl-phenols (I: R=Me) furnished on migration 2 methyl- and 3-methyl-4-cinnamoylphenols (II: R=Me) respectively, identified by comparing with the condensation products of 2-methyl- and 3-methyl-4-acetylphenols (III: R=Me), obtained by the Fries shifts of the corresponding cresyl acetates (Rosenmund and Schnurr, *loc. cit.*, Beri *et al.*, *Proc. Ind. Acad. Sci.*, 1951, **33A**, 88 ; Cullinane and Edwards, *J. Chem. Soc.* 1958, 434) with benzaldehyde in presence of alkali (cf. Neurath, *Monatsh.*, 1906, **27**, 1148 ; Kohler and Heritage *J. Amer. Chem. Soc.*, 1911, **33**, 30). 4-Methylphenyl cinnamate, however, did not rearrange under several experimental conditions ; some cinnamic acid and a pasty intractable material were obtained. This is in confirmation with the observation of Rosenmund and Schnurr (*loc. cit.*).

4-Chloro-5-methylphenyl cinnamate (IV: R=Me ; X=Cl) isomerised by the action of aluminium chloride to 3-chloro-5-methyl-2 cinnamoylphenol (V: R=Me ; X=Cl) since the *para* position was blocked. The constitution was confirmed by a direct

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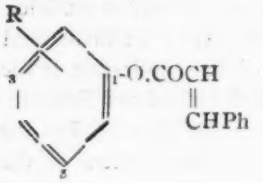
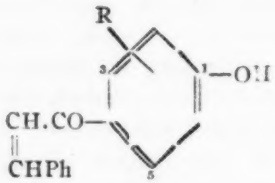
comparison with the chalkone derivative produced by the condensation of 4-chloro-5-methyl-2-acetylphenol (VI: R=Me; X=Cl) and benzaldehyde (Ghadawala and Amin, unpublished). Similarly, 4-benzoylphenyl cinnamate (IV: R=H; X=COPh) also afforded 4-benzoyl-2-cinnamoylphenol (V: R=H; X=COPh), which was also prepared by the condensation of 4-benzoyl-2-acetylphenol (VI: R=H; X=COPh) with benzaydehyde (Joshi *et al.*, *Science & Culture.*, 1957, **23**, 199).

The cinnamates of 2-chloro-, 2:4-dichloro- and 2:4-dibromo-phenols and 1-naphthyl cinnamate did.not rearrange under several experimental conditions; only uncrystallisable pasty masses along with some cinnamic acid were recovered in these cases.

It is significant that the reaction of phenyl cinnamate is prevented by the presence of a methyl group in 4-position, while the benzoyl group in the same position does not hinder. However, in all the cases the yields of the cinnamoylphenols were quite satisfactory. This is also an additional method of preparing hydroxy-chalkones.



(I)



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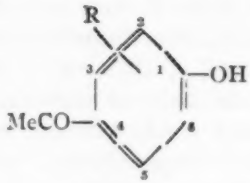

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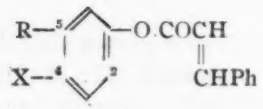
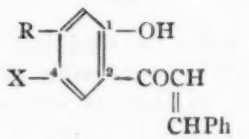
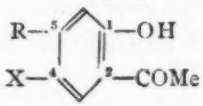


(IV)



(V)



(VI)

EXPERIMENTAL

Phenyl cinnamate (I: R=H) was prepared by the following simplified procedure. A mixture of cinnamic acid (0.5 *M*) and thionyl chloride (0.5*M*) was heated on a water-bath till HCl gas had ceased to evolve (about 1½ hours). The freshly distilled phenol (0.5 *M*) was added and heating was continued for another hour, followed by heating for about 30 minutes on a wire gauze. Finally, the reaction mixture was cooled and poured into ice. The solid was filtered, washed with sodium bicarbonate (5 %) to remove the excess acid, if any, and crystallised from ethanol, m.p. 75-76°, yield 70% [cf. "Organic Synthesis", 1940, Vol, 20 p. 77].

Fries Rearrangement: Formation of 4-Cinnamoylphenol (II: R=H).—The ester (I: R=H; 3 g., 1 *M*) was added to a solution of anhydrous aluminium chloride (5.9 g., 3.3 *M*) in dry nitrobenzene (25 c.c.); the brownish reaction mixture was left overnight at room temperature (25-30°). The reaction mixture was then treated with ice and HCl (5 c.c.) and the solvent removed by steam-distillation. The hot residual liquid was filtered. The filtrate on cooling deposited a brownish solid which was crystallised from ethanol in orange needles, m.p. 173-74°. A further small quantity

of the product was obtained by extracting the tarry mass with ethyl acetate (total yield 0.80-85 g.). The mixed melting point with an authentic sample of 4-cinnamoylphenol, prepared from 4-acetylphenol (III: R=H ; Norris and Sturgis, *J. Amer. Chem. Soc.*, 1939, **61**, 1413) remained undepressed. It is soluble in common organic solvents and sodium hydroxide. It develops a deep red colour with violet tinge with H_2SO_4 (conc.).

TABLE I

4'-Cinnamoylphenol.

Expt. No.	Temp.	Time.	Solvent.	Yield.
1.	70°	4 hrs.	Nil	...
2.	100°	2	Nil	...
3.	60°	2	Nitrobenzene (25 c.c.)	0.15 g.
4.	25-30°	24	Do	0.85
5.	25-30°	24	Nitrobenzene (25 c.c.)+2.2 *M*-$AlCl_3$	0.60
6.	25-30°	24	Nitrobenzene (25 c.c.)+1.1 *M*-$AlCl_3$	...

Note : (a) In Expt. No. 1 and No. 6 unchanged phenyl cinnamate (0.8-1.0 g.) was recovered.
(b) Tarry pasty mass in variable amounts was recovered in all cases from which no definite product could be obtained.

The *benzoate*, prepared by benzoyl chloride-pyridine method, was crystallised from ethanol in colorless needles, m.p. 139°. (Found: C, 80.20; H, 4.57. $C_{22}H_{16}O_3$ requires C, 80.40; H, 4.87%).

The *methoxy derivative*, prepared by dimethyl sulphate-potassium carbonate-acetone method, was crystallised from ethanol in long needles, m.p. 110°. [Found: C, 80.46; H, 5.56. $C_{16}H_{14}O_3$ requires C, 80.67; H, 5.88%].

Table I records other conditions under which the rearrangement was studied. Table II records the characteristics and the analytical data of the phenyl cinnamates.

TABLE II

Phenyl cinnamates.

Serial No.	Phenyl cinnamate.	Cryst. appearance.	M.P.	Formula.	Found	Calc.
1.	2-Methyl	Yellowish granules (E)	85°	$C_{16}H_{14}O_2$		
2.	3-Methyl	White granules (E)	65°	$C_{16}H_{14}O_2$		
3.	4-Methyl	Yellowish granules (E)	102°	$C_{16}H_{14}O_2$		
4.	4-Chloro-5-methyl	Brownish shining plates (E)	94°	$C_{16}H_{13}O_2Cl$		
5.	4-Benzoyl	Yellowish plates (E)	118°	$C_{22}H_{16}O_3$	C: 80.22	80.48
					H: 4.69	4.91
6.	2-Chloro	Yellowish powder (E)	81°	$C_{15}H_{11}O_2Cl$	Cl: 13.43	13.73
7.	2:4-Dichloro	Pale brown granules (B)	95°	$C_{15}H_{10}O_2Cl_2$	Cl: 23.93	24.19
8.	2:4-Dibromo	White granules (E)	106°	$C_{15}H_{10}O_2Br_2$	Br: 41.73	41.88
9.	1-Naphthyl	Violet granules (B)	111°	$C_{19}H_{14}O_2$		

Note : (E) = Ethanol. (B) = Benzene.
The cinnamates No. 1, 2, 3, 4 and 9 are described in literature (Beilstein, IX, pp. 584-85).

Characteristics and analytical data of the cinnamoylphenols obtained by the Fries rearrangement of cinnamates and their benzoyl derivatives are recorded respectively in Tables III and IV.

TABLE III

Serial No.	Cinnamoylphenol.	Cryst. appearance.	M.P.	Yield.	% Carbon. Found.	% Carbon. Calc	% Hydrogen. Found.	% Hydrogen. Calc.
*A	2-Methyl-4-	Violet plates (B)	155°	1.3 g.	80.46	80.67	5.64	5.88
B	3-Methyl-4-	Light orange plates (B)	126°	1.8	80.43	80.67	5.69	5.88
**C	4-Chloro-5-methyl-2-	Glistening yellow needles (A)	142°	1.0	...	...	...	...
D	4-Benzoyl-2-	Light yellow needles (A)	128°	1.0	80.31	80.48	4.73	4.91

* Neurath (*loc. cit.*) records m.p. 137° for 'A'.
** In compound C, only chlorine was estimated. (Found : Cl, 12.99; calc. 13.05%).

TABLE IV

Serial No.	Benzoyl derivative of	Colour and shape of crystals.	M.P.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
1.	A	Discoloured granules (E)	100°	$C_{23}H_{18}O_3$	80.43	80.71	5.02	5.26
2.	B	White granules (E)	102°	$C_{23}H_{18}O_3$	80.37	80.71	5.05	5.26
3.	*C	Pale yellow, small needles (A)	98°	$C_{23}H_{17}O_3Cl$	...	...	...	...
4.	D	Pale yellow, short needles (A)	134°	$C_{29}H_{20}O_4$	80.26	80.56	4.41	4.62

* In C, only chlorine was estimated. (Found : Cl, 9.48; calc. 9.44%).
Note : (A) = Acetic acid. (B) = Benzene. (E) = Ethanol.

One of the authors (C.M.C.) thanks the Ministry of Education, Government of India for the award of a senior research scholarship.

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Received April 13, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

CHEMISTRY OF MONOFLUOROARSENATES

By Asimbikash Ray and Grihapati Mitra

The chemistry of monofluoroarsenates has been described. AsO_3F^{2-} ion bears a strong resemblance with the SO_4^{2-} ion. Pure salts of alkali, alkaline earth and heavy metals have been prepared. Double salts of the type M'_2M'' $(AsO_3F)_2,6H_2O$ and complex salts with NH_3 and organic bases have also been prepared. Most of the monofluoroarsenates are more soluble than the corresponding sulphates. Monofluoroarsenates form mixed crystals with sulphates. X-ray analysis has, however, revealed that $ZnAsO_3F,6H_2O$ is not isomorphous with the corresponding sulphate. In a very dilute solution and in presence of excess of acid, pentavalent arsenic in AsO_3F^{2-} is almost quantitatively reduced to trivalent arsenic by KI. The precipitation of silver arsenate by the addition of silver nitrate solution to a soluble monofluoroarsenate is not quantitative.

Phosphorus forms three well-defined anions with fluorine, e.g., PO_3F^{2-}, $PO_2F_2^-$ and PF_6^- (Lange, "Fluorine Chemistry", Vol, I, edited by J. H. Simons, Academic Press Inc., New York, 1950, pp. 126-189). Though arsenic in its chemical properties bears a strong resemblance with phosphorus, the corresponding oxyfluoro anions of arsenic have not been reported. The hexafluoroarsenates, e.g., the salts of AsF_6^- ion, are, however, known for a long time (Lange and Askitopoulos, *Z. anorg. Chem.*, 1935, **223**, 369). In the literature, a comparatively little known compound, potassium oxytetrafluoroarsenate, $KAsOF_4,H_2O$, is also mentioned to have been obtained as rhombic plates from a solution of potassium arsenate, dissolved in dilute hydrofluoric acid (Marignac, *Bull. Soc. Chim.*, 1947, **8**, 327).

Recently the mono- and the difluoroarsenates have been reported by us (*Science & Culture*, 1953, **19**, 216; 1955, **20**, 404). The chemistry of difluoroarsenates has already been described in details (this *Journal*, 1959, **36**, 559). The present parer deals with the methods of preparation and properties of monofluoroarsenates.

Dutt and Gupta have recently described a large number of monofluoroarsenates prepared by a different method (*Z. anorg. allgem. Chem.*, 1957, **285**, 92). More recently Kolditz and Rohnsch (*ibid.*, 1957, **293**, 168) have reported failure to isolate monofluoroarsenate by the method described by Dutt and Gupta. Our observations, though the methods of preparation are different, however, support strongly the claim of Dutt and Gupta (*loc. cit.*). The chemical composition as well as observed properties of these compounds are in good agreement with those claimed by Dutt and Gupta.

It is of interest to note that arsenyl fluoride, $AsOF_3$, the anhydride of these two anions, has also been reported recently by one of us (Mitra, *J. Amer. Chem. Soc.*, 1958, **80**, 5639).

Experimental

Fluorine in the compounds was estimated as calcium fluoride. A weighed amount of the substance was fused with sodium carbonate in a crucible The mass left

was leached with hot water and the resulting solution was filtered. The amount of fluoride ion present in the filtrate was determined gravimetrically as CaF_2.

After removal of fluorine, either as CaF_2 or by heating the original substance with concentrated acid, the other constituents were determined, following the usual standard methods.

The simple salts were prepared by the following three methods.

(*a*). Soluble monofluoroarsenates were obtained by digesting in a platinum basin equimolecular amounts of the metal fluoride, metal hydroxide and arsenic pentoxide (obtained by oxidising As_2O_3 with nitric acid) according to the equation :

$$MF_2 = M(OH)_2 + As_2O_5 = 2MAsO_3F + H_2O$$

where, M = Zn, Cd, Cu, Ni etc. The whole mixture was warmed in a platinum basin on the water-bath and glacial acid or HNO_3 (conc.) was added dropwise with constant stirring till an almost clear solution was obtained. It was then digested on the water-bath for about an hour. The solution was filtered after cooling in order to remove any insoluble matter. Well-defined crystals appeared when the solutions were concentrated in a vacuum desiccator (H_2SO_4). The following compounds were isolated by this method.

Copper monofluoroarsenate pentahydrate: (Found : Cu, 21.42 ; As, 25.38 ; F, 6.32. $CuAsO_3F,5H_2O$ requires Cu, 21.49 ; As, 25.71 ; F, 6.43%).

Zinc monofluoroarsenate heptahydrate: (Found : Zn, 19.43; As, 22.09 ; F, 5.37. $ZnAsO_3F, 7H_2O$ requires Zn, 19.60 ; As, 22.46 ; F, 5.70%).

Nickel monofluoroarsenate heptahydrate : (Found : Ni, 17.91 ; As, 22.81 ; F, 5.66. $NiAsO_3F,7H_2O$ requires Ni, 17.96; As, 22.94 ; F, 5.82%).

Cadmium monofluoroarsenate 8/3 *hydrate* : (Found : Cd, 36.85; As, 24.39 ; F, 6.07. $CdAsO_3F,8/3\ H_2O$ requires Cd, 37.17 ; As, 24.78 ; F, 6.28%).

(*b*). The alkali salts were found difficult to prepare. Rubidium monofluoroarsenate was prepared by passing $AsOF_3$ through cold RbOH solution, kept in a platinum basin, immersed in ice and salt. Rubidium difluoroarsenate, which was found to be the major product, crystallised out at first. From the very concentrated solution rubidium monofluoroarsenate crystallised out. (Found: Rb, 54.33 ; As, 23.58 ; F, 5.79. Rb_2AsO_2F requires Rb, 54.65 ; As, 23.95 ; F, 6.07%).

(*c*). The insoluble monofluoroarsenates were prepared by double decomposition between a soluble monofluoroarsenate and a soluble salt of the metal. The reaction was carried out at a low temperature. Addition of a few drops of amyl alcohol afforded better results during precipitation from a dilute solution. This perhaps suppressed the secondary reaction :

$$AsO_3F + H_2O \rightleftharpoons AsO_3OH + HF.$$

Barium and lead compounds have been isolated by this method.

Barium monofluoroarsenate : (Found : Ba, 49.23 ; As, 26.40 ; F, 6.49. $BaAsO_3F$ requires Ba, 49.18 ; As, 26.82 ; F, 6.80%).

Lead monofluoroarsenate: (Found: Pb, 59.07; As, 21.53; F, 5.39. $PbAsO_3F$ requires Pb, 59.35; As, 21.47; F, 5.44%).

It is of interest to note that the free acid, H_2AsO_3F, has not been isolated as yet. The difluoroarsenic acid, $HAsO_2F_2$ has, however, been isolated by us (*loc. cit.*).

Solubilities.—Monofluoroarsenates of the divalent metals are, in general, more soluble than the corresponding sulphates. Even a saturated solution of the sparingly soluble $BaAsO_3F$ or $PbAsO_3F$ affords quite an appreciable amount of the white precipitate of $BaSO_4$ or $PbSO_4$ by the addition of potassium sulphate solution.

Structure.—Monofluoroarsenates, in general, form mixed crystals with the divalent ions, such as, SO_4^{2-}, BeF_4^{2-}, PO_3F^{2-}, ClO_3F^{2-} etc. (Mitra and Ray, *Science & Culture*, 1956, **21**, 379). It is noteworthy that in these series of anions the A—F or A—O distances (where A=S, Be, P or Cl) are very close to one another and to those of As—O and As—F in AsO_2F^{2-} ion. In addition, all of these complex anions are divalent. All of them, however, do not give rise to regular tetrahedra (*loc. cit.*), but mixed crystals are formed very easily.

The powder picture of $ZnAsO_3F,6H_2O$ exhibits a very strong line at 4.950Å, strong lines at 4.097 and 2.547Å and medium strong lines at 1.873 and 1.627Å. The *d* values are given in K units. This compound, when compared with the standard spacings given for $ZnSO_4, 6H_2O$, is not found isomorphous with those of the corresponding sulphate. Hence, zinc monofluoroarsenate has a different structure. The As—F link has already been reported to be appreciably ionic in nature (Pauling, "The Nature of Chemical Bond"). This might have resulted in an appreciable distortion in the resulting tetrahedral structure or the inertness of the 4*s* electrons of arsenic might have caused hybridisation of the 4*p* electrons with the 4*d* level. Further investigations are required to confirm the results.

Chemical Properties.—Not only in chemical compositions but also in their properties, the monofluoroarsenates bear a strong resemblance with the corresponding sulphates. Ni, Zn and Co salts have been found to crystallise with both seven as well as six molecules of water. The hydrous monofluoroarsenates of Cu, Ni and Zn etc. have not been isolated as yet.

The sparingly soluble $BaAsO_3F$ or $PbAsO_3F$ is precipitated from a concentrated solution of any soluble monofluoroarsenate without any contamination with the metal fluoride. The monofluoroarsenates of Ca and Mg have not been prepared in their purest forms.

Monofluoroarsenates of Zn, Ni etc. form a series of double salts analogous in composition to the corresponding Tuttion's salts, formed by the sulphates. Pure alums of monofluoroarsenate ion have, however, not yet been prepared.

Monofluoroarsenates of various metals yield complexes with ammonia, like tetrammino-cupric monofluoroarsenate monohydrate, $[Cu(NH_3)_4],H_2O$ etc. Similar complexes have also been prepared with organic bases like pyridine, etc.

The monofluoroarsenate ion liberates iodine from KI only in acidic solution and the following reaction almost goes to completion in a dilute solution containing excess of acid.

$$As^{5+} + 2KI = I_2 + As^{3+} + 2K^+.$$

A solution of silver nitrate precipitates chocolate-coloured silver arsenate. This is the reason why silver monofluoroarsenate has not been isolated as yet. The precipitation of silver arsenate is, however, not quantitative.

The authors are grateful to Prof. N. N. Ray, formerly of the Presidency College, Culcutta, and to Prof. G. H. Cady of the University of Washington, Seattle, for their kind patronage and also for providing laboratory facilities during the progress of this work.

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Received December 12, 1958.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

REACTION OF AROMATIC ALDEHYDES WITH 5-METHYL-4-THIAZOLIDONES

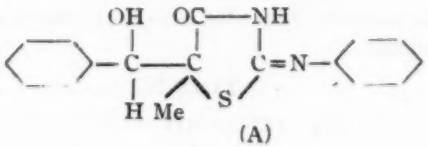
By A. S. Mittra and M. K. Rout

Several 5-methyl-2-arylimino-4-thiazolidones, prepared by the action of α-chloropropionic acid on monosubstituted thioureas, have been condensed with aromatic aldehydes, and the nature of the products has been investigated. Aldol type of compounds has been found to be formed by the action of aromatic aldehydes on 5-methyl-4-thiazolidones.

Several 5-methyl-2-arylimino-4-thiazolidones have been obtained by the condensation of α-chloropropionic acid with monosubstituted thioureas in good yields according to the method of Rout *et al.* (*J. Amer. Chem. Soc.*, 1955, **77**, 2427). The sulphur is found to be firmly held in these compounds. The ultraviolet absorption spectrum of 5-methyl-2-phenylimino-4-thiazolidone is found to be similar to that of 2-phenylimino-4-thiazolidone, as is expected, and the both show λ_{max} at 268 mμ in methyl alcoholic solution. The properties of the thiazolidones together with their melting points and analytical values are recorded in Table I.

The condensation of 5-methyl-2-arylimino-4-thiazolidones with aromatic aldehydes has been investigated. Benzaldehyde condenses with 5-methyl-2-phenylimino-4-thiazolidone in glacial acetic acid medium in the presence of fused sodium acetate. *p*-Dimethylaminobenzaldehyde reacts with the above 5-methyl-2-phenylimino-4-thiazolidone in the presence of piperidine in alcoholic solution.

Benzaldehyde is found to condense with 5-methyl-2-phenylimino-4-thiazolidone in aqueous ethyl alcohol in the presence of piperidine—a condition known to favour aldol formation (Philips, *ibid.*, 1945, **67**, 744)—to yield a product identical with the condensation product formed in acetic acid medium. The above condensation product forms an acetate on treatment with acetic anhydride in the presence of pyridine. In view of the above observations an aldol structure (A) has been assigned to the product of the reaction between aromatic aldehydes and 5-methyl-2-phenylimino-4-thiazolidone.



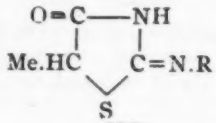
(A)

Experimental

5-Methyl-2-phenylimino-4-thiazolidone.—α-Chloropropionic acid (10 g.) and phenylthiourea (10 g.) were dissolved in absolute alcohol (30 c.c.); fused sodium acetate (10 g.) was added and the mixture was refluxed for 6 hours on a water-bath.

Alcohol was boiled off and water was added to the cooled residue. The product separated out as a gum which solidified on keeping in contact with water for 24 hours. It was repeatedly washed with water and crystallised from methyl alcohol as pale yellow rice-grain shaped crystals, m.p. 136°, yield 11.5 g. (Found: S, 15.19. $C_{10}H_{10}ON_2S$ requires S, 15.53%).

TABLE I

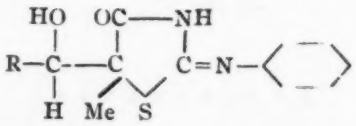


Substituent.	Colour.	M.P.	Yield.	% Sulphur. Found.	Calc.
Phenyl	Pale yellow	136°	65%	15.19	15.53
p-Tolyl	Pale yellow	141°	65	14.31	14.54
m-Chlorophenyl	Colorless	152°	60	12.99	13.33
p-Nitrophenyl	Yellowish red	190°	60	12.46	12.74
α-Naphthyl	Bluish white	150°	60	12.20	12.50

Condensation with Benzaldehyde.—(*a*). The thiazolidone (5 g.), benzaldehyde (3 g.) and fused sodium acetate (3 g.) in glacial acetic acid (10 c.c.) were refluxed over asbestos-wire gauze for 2 hours and then poured into water. The product settled down as a gum. It was separated by decantation, washed repeatedly with water and then treated with hot methyl alcohol. The residue, insoluble in methyl alcohol, was filtered off. The methyl alcoholic solution yielded, on keeping for a day, a crop of pale yellow crystals. The insouble residue and the first crop of crystals were found to be identical. It was recrystallised from chloroform, m.p. 181°, yield 2.5 g. (Found: S, 10.32. Aldol $C_{17}H_{16}O_2N_2S$ requires S, 10.02%).

(*b*). The thiazolidone (1 g.) was refluxed with benzaldehyde (0.5g.) for 6 hours along with three drops of piperidine in rectified spirit (25 c.c.). The alcohol was boiled off and water was added to the residue when a gum separated out. It was dissolved in hot methyl alcohol; a small quantity of crystals separated from the solution next day. The crystals were recrystallised from chloroform, m.p. 181°, yield 0.1 g. In Table II are recorded the physical properties and analytical data of some of the products of reaction between aromatic aldehydes and 5-methyl-2-phenylimino-4-thiazolidone.

TABLE II



R.	Colour of aldol.	M.P.	% Sulphur. Found.	Calc.
o-Chlorophenyl	Colorless	165°	10.42	10.19
p-Nitrophenyl	Yellowish red	187°	9.61	9.84
p-Dimethylaminophenyl	Yellowish red	161°	8.92	9.01

The chloro- and nitrobenzaldehydes reacted in acetic acid medium in the presence of sodium acetate. *p*-Dimethylaminobenzaldehyde furnished no crystallisable product in acetic acid medium and the aldol was obtained from it in alcoholic medium in the presence ot piperidine.

Acetate of Aldol.—The aldol (0.5 g.) of 5-methyl-2-phenylimino-4-thiazolidone and benzaldehyde was dissolved in pyridine (2 c.c.) and to this solution acetic anhydride (2 c.c.) was added and the mixture was allowed to stand for 24 hours. The mixture was treated with ice-cold HCl (dil.) and the precipitate was crystallised from methyl alcohol, m.p. 172°, yield 0.3 g. (Found: CO.Me, 12.32. $C_{17}H_{13}ON_2SO.OC.CH_3$ requires CO.Me, 12.14%).

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Received November 20, 1958.

[Jour. Indian Chem. Soc, Vol. 36, No. 10, 1959]

STUDIES IN CHALKONES AND RELATED COMPOUNDS DERIVED FROM CHLORO-SUBSTITUTED HYDROXYACETOPHENONES. PART I. SYNTHESIS OF CHALKONES

By N. M. Shah and S. R. Parikh

Various chalkones, derived from 4-hydroxy-3 chloro- and 2-hydroxy-3-, -4- or -5-chloro-acetophenones are described. The dibromides of the chalkones have been studied; on alkaline hydrolysis of the dibromides, the corresponding benzylidene-coumaranones have been obtained.

Various halogenated acetophenones, particularly *ortho*-hydroxy ones now easily available by the Fries migration of isomeric chlorophenyl acetates (Shah and Parikh, this *issue*, p. 729), are useful substances for synthesising chalkones and related compounds. As a part of this study, the present work was undertaken. The various chalkones derived from 4-hydroxy-3-chloro- and 2-hydroxy-3-, -4- and -5-chloro-acetophenones have been described herein.

2′-Hydroxy-3′-, -4′- and -5-chloro-chalkones were treated with bromine in acetic acid, when their dibromides were obtained. The latter on treatment with potassium iodide in acetone were debrominated, the original chalkones having been obtained. It is interesting to note that 2:2′-dihydroxy-3′-chloro- and -5′-chlorochalkones on similar bromination afford a monobromo derivative, which does not regenerate the original chalkone with potassium iodide treatment.

The above dibromides were treated with alcoholic potassium hydroxide, when 7-, 6- and 5-chlorobenzylidene-coumaranones were obtained instead of the corresponding flavones The synthesis of these flavones forms the succeeding part of the series (*loc. cit.*).

Experimental

General Method of Chalkone Formation.—An alcoholic solution of the appropriate ketone was mixed with the aldehyde, and KOH (40%) was carefully added with shaking. The reaction mixture was allowed to stand at room temperature for a period varying from 12 to 24 hours, depending on the nature of the ketone used. It was then poured into ice and acidified. The chalkone was collected and crystallised from alcohol. Various chalkones, prepared as above from different ketones, are recorded in Table I.

Dibromide Formation.—The chalkone, dissolved in glacial acetic acid, was treated with bromine. The clear red solution was left aside for nearly 24 hours at room temperature and then it was treated with water. The product was collected, washed with water and crystallised from alcohol. The dibromides formed (Table II) were refluxed with KI in acetone solution. The products were found to be the original chalkones by mixed melting points.

TABLE I

	Aldehydes.	Chalkones.	Cryst. form.	M.P.	Found.	Calc.
	(I). Chalkones derived from 4-hydroxy-3-chloroacetophenone (Ch = 3′-chlorochalkone).					
1.	Benzaldehyde	4′-Hydroxy-Ch ($C_{15}H_{11}O_2Cl$)	Yellow granules	163° (shrinks at 155°)	Cl: 13.70 C: 69.45 H: 4.30	13.73 69.64 4.25
2.	Anisaldehyde	4′-Hydroxy-4-methoxy-Ch ($C_{16}H_{13}O_3Cl$)	Yellow needles	200°	Cl: 12.24 C: 66.43 H: 4.41	12.34 66.55 4.50
	Methoxy derivative	...	Needles	135°	Cl: 11.70	11.76
3.	Salicylaldehyde	2:4′-Dihydroxy-Ch ($C_{15}H_{11}O_3Cl$)	Yellow granules	85°	Cl: 13.00 C: 65.46 H: 3.91	12.93 65.53 4.01
	Methoxy derivative	...	Greenish ,,	130°	Cl: 12.28	12.30
4.	Piperonal	4′-Hydroxy-3:4-methylenedioxy-Ch ($C_{16}H_{11}O_4Cl$)	Yellow ,,	223°	Cl: 11.68 C: 63.40 H: 3.56	11.73 63.47 3.64
	Methoxy derivative	...	Yellow ,,	152°	Cl: 11.16	11.21
5.	Vanillin	4:4′-Dihydroxy-3-methoxy-Ch ($C_{16}H_{13}O_4Cl$)	Yellow needles	94°	Cl: 11.58 C: 63.00 H: 4.12	11.66 63.03 4.17
	Methoxy derivative	...	Needles	64°	Cl: 11.11	11.15
	N. B. The methoxy derivatives were prepared by dimethyl sulphate-acetone-K_2CO_3 method. The chalkones developed no colour with EtOH—$FeCl_3$ and a greenish yellow colour in alkali.					
	(II). Chalkones from 2-hydroxy-3-chloroacetophenone (Ch = 3′-chlorochalkone).					
1.	Benzaldehyde	2′-Hydroxy-Ch ($C_{15}H_{11}O_2Cl$)	Yellow needles	118-19°	Cl: 13.70 C: 69.43 H: 4.20	13.73 69.64 4.25
	Methoxy derivative	...	Granules	140°	Cl: 12.98	13.01
	Acetoxy derivative	...	,,	55-57°	Cl: 11.78	11.51
2.	Salicylaldehyde	2:2′-Dihydroxy-Ch* ($C_{15}H_{11}O_3Cl$)	Yellow granules	180-81°	Cl: 12.88 C: 65.46 H: 3.93	12.93 65.53 4.01
		*The yield is extremely poor.				
	(III). Chalkones from 2-hydroxy-5-chloroacetophenone (Ch = 5′-chlorochalkone).					
1.	Benzaldehyde	2′-Hydroxy-Ch ($C_{15}H_{11}O_2Cl$)	Yellow granules	105°*		
	Acetoxy derivative	...	Needles	198°	Cl: 11.70	11.81
	Benzoyl derivative	...	Granules (shrinks at 170°)	178°	Cl: 9.64	9.79
2.	Salicylaldehyde	2′:2-Dihydroxy-Ch ($C_{15}H_{11}O_3Cl$)	Yellow granules	160°	Cl: 12.79	12.93
	Methoxy derivative	...	Yellowish granules	125°	Cl: 12.28	12.30
		* Kunckell (*Ber.*, 1911, **44**, 5654) reports m.p. 107°.				
	(IV) Chalkones from 2-hydroxy-4-chloroacetophenone (Ch = 4′-chlorochalkone)					
1.	Benzaldehyde	2′-Hydroxy-Ch ($C_{15}H_{11}O_2Cl$)	Yellow needles	125°	Cl: 13.73	13.63
	Acetoxy derivative		Rhombic plates	90°	Cl: 11.80	11.81

TABLE II

[Ch denotes chlorochalkone]

	Cryst. form.	M.P.	Found.	Calc.
(*a*). Dibromides :				
2-Hydroxy-3-Ch ($C_{15}H_{11}O_2ClBr_2$)	Yellow needles	158° (shrinks at 120°)	Br : 38.18 Cl : 8.45	38.23 8.48
2′-Hydroxy-4′-Ch	Do	180°	Br : 38.19 Cl : 8.47	38.23 8.48
2′-Hydroxy-5′-Ch	Do	184°*		
(*b*). Benzylidene-coumaranones :				
6-Chloro-($C_{15}H_9O_2Cl$)	Brown needles	195°**	Cl : 13.77	13 84
7-Chloro-	Yellow needles	120°**	Cl : 13.79	13.84
5-Chloro-	Yellow granules	154°**	Cl : 13.77	13.84

*Kunckell (*loc. cit.*) records m.p. 185°

** The mixed melting points of these coumaranones with authentic samples of the corresponding flavones were depressed.

2 : 2′-*Dihydroxy*-3′-*chlorochalkone* on similar treatment furnished red short needles, m.p. 245°. (Found : Cl, 9.92 ; Br, 22.38. $C_{15}H_{10}O_3ClBr$ requires Cl, 10.04 ; Br, 22.62%).

2 : 2′-*Dihydroxy*-5′-*chlorochalkone* similarly afforded red needles, m.p. 215° (decomp.). (Found : Cl, 10.0 ; Br, 22.54. $C_{15}H_{10}O_3ClBr$ requires Cl, 10.04 ; Br, 22.62%).

Both the monobromo derivatives could not be debrominated by acetonic potassium iodide. Hence, it appears that bromine has entered the benzene nucleus.

Hydrolysis of Chalkone Dibromides.—The above chalkone dibromides were refluxed with alcoholic KOH (1 g. in 30 c.c.) for 2 hours. The cooled solution was acidified and the product crystallised from alcohol. The benzylidene-coumaranones are recorded in Table II.

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Received February 2, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

STUDIES IN CHALKONES AND RELATED COMPOUNDS DERIVED FROM CHLORO-SUBSTITUTED HYDROXYACETOPHENONES. PART II. FLAVONES AND FLAVONOLS.

By S. R. Parikh and N. M. Shah

By the selenium dioxide (Venkataraman) oxidation and the alkaline hydrogen peroxide (Algar-Flynn) oxidation of some chlorochalkones, the corresponding chlorine-containing flavones and flavonols respectively have been synthesised.

The derivation of various chalkones from differently chlorine-substituted 2-hydroxyacetophenones and the alkaline hydrolysis of their dibromides, yielding benzylidene-coumaranones instead of the expected flavones (vide Part I), have now been extended to the synthesis of other heterocyclic compounds. The synthesis of flavanones, flavones and flavonols from these chalkones is described in this communication.

When 2′-hydroxy-5′-, 2 : 2′-dihydroxy-5′-, 2′-hydroxy-4′- and 2′-hydroxy-3′-chloro-chalkones were subjected to selenium dioxide oxidation (Venkataraman *et al.*, *J. Chem. Soc.*, 1935, 866 ; 1936, 569) in dry amyl alcohol, 6-chloro-, 6-chloro-2′-hydroxy-, 7-chloro- and 8-chloro-flavones respectively were obtained. 2′-Hydroxy-3′-chloro-chalkone was cyclised to 8-chloroflavanone by hydrochloric acid (10%) and the flavanone was then oxidised to 8-chloroflavone by selenium dioxide. 2′-Hydroxy-4′-chloro-chalkone could not be cyclised to 7-chloroflavanone, but on oxidation with selenium dioxide it afforded directly 7-chloroflavone.

2 : 2′-Dihydroxy-5′-chlorochalkone was cyclised to 6-chloro-2′-hydroxyflavanone, which on selenium dioxide oxidation furnished 6-chloro-2′-hydroxyflavone.

The above chalkones were then subjected to the Algar-Flynn oxidation (*Proc. Roy. Irish Acad.*, 1934, **B42**, 1) using alkaline hydrogen peroxide. Under these conditions 6-chloro-, 6-chloro-2′-hydroxy-, 7-chloro- and 8-chloro-flavonols were obtained.

Experimental

General Procedure.—A mixture of the chalkone (1 g.) and selenium dioxide (1 g.) in dry *iso*amyl alcohol (15 c.c.) was refluxed in an oil-bath at 130-40° for 8 hours. The precipitated selenium was filtered off and the filtrate steam-distilled to remove the alcohol. A brown product remaining in the flask was collected and crystallised from alcohol. The flavones prepared are recorded in Table I.

Table I

Chalkone.	Flavone.	Cryst. form.	M.P.	% Chlorine.	
				Found.	Calc.
2′-Hydroxy 3′-chloro-	8-Chloro-flavone ($C_{15}H_9O_2Cl$)	Cluster of needles	167°	13.81	13.84
2′-Hydroxy-4′-chloro-	7-Chloro-	Colorless granules	151°	13.60	13.84
2′-Hydroxy-5′-chloro-	6-Chloro-	Yellowish granules	184°	13.79	13.84
2 : 2′-Dihydroxy-5′-chloro-	6-Chloro-2′-hydroxy-	Do	228-29°	12.97	13.02

8-Chloro-, 6-chloro- and 6-chloro-2′-hydroxy-flavanones, described below, were similarly subjected to the above selenium dioxide oxidation, when 8-chloro-, 6-chloro- and 6-chloro-2′-hydroxy-flavones were respectively obtained.

Flavanone Formation.—2′-Hydroxy-3′-chlorochalkone (0.5 g.) in alcohol (5 c.c.) was treated with HCl (7 c.c., 10%), when a white turbidity appeared. It was dissolved by adding more alcohol (10-15 c.c.) and the solution was refluxed on a water-bath for 24 hours. Alcohol was then distilled off and the residue extracted with ether. On removal of the ether, the product was crystallised from alcohol in yellowish needles, m.p. 121°. 8-Chloroflavanone is insoluble in alkali and depresses the m.p. of the chalkone. (Found: Cl, 13.61. $C_{15}H_{11}O_2Cl$ requires Cl, 13.68%).

Similarly, 2′-hydroxy-5′-chlorochalkone was cyclised to 6-chloroflavanone by HCl-treatment as above. It was crystallised from alcohol in yellowish needles, m.p. 89°. (Found: Cl, 13.47. $C_{15}H_{11}O_2Cl$ requires Cl, 13.68%). The flavanone does not dissolve in alkali.

2 : 2′-Dihydroxy-5′-chlorochalkone was similarly cyclised to 6-chloro-2′-hydroxy-flavanone, which crystallised from alcohol in greenish granules, m.p. 150-51°. (Found: Cl, 12.90. $C_{15}H_{11}O_3Cl$ requires Cl, 12.93%).

All attempts to cyclise 2′-hydroxy-4′-chloro- and 2 : 2′-dihydroxy-3′-chloro-chalkones to the corresponding flavanones were unsuccessful.

Flavonol Formation (Algar-Flynn Oxidation).—The chalkone (0.5 g.) was mixed with NaOH (15 c.c., 10%) and then methyl alcohol (15 c.c.) was added. The mixture was warmed, if necessary, to obtain a clear solution; it was cooled in ice, H_2O_2 (4 c.c., 18%) was added, and left in an ice-bath for 2 hours, and then overnight at room temperature. It turned yellow. It was poured into ice-water and acidified. The substance was collected and crystallised from alcohol. The flavonols, thus obtained, are recorded in Table II.

TABLE II

Chalkone.	Flavonol.	Cryst form.	M.P.	% Chlorine. Found.	Calc.
2′-Hydroxy-3′-chloro-	8-Chloro-	Lustrous needles	190°	13.16	13.03
2′-Hydroxy-4′-chloro-	7-Chloro-	Lustrous plates	181°	12.95	13.03
2′-Hydroxy-5′-chloro-	6-Chloro-	Colorless granules	165-66°	12.92	13.03
2 : 2′-Dihydroxy-5′-chloro-	6-Chloro-2′-hydroxy-	Shining short needles	222-23°	12.23	12.26

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Received February 2, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

THIAZOLIDONES. PART II

By K. J. Shah, K. C. Kshatriya and J. J. Trivedi

2-Benzylimino-4-thiazolidones have been synthesised from substituted benzylthioureas and condensed with various aldehydes.

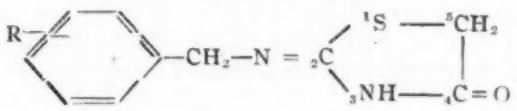
The purpose of synthesising 2-benzylimino-4-thiazolidones and the preparation of some of these have been described in Part I (Trivedi *et al.*, this *Journal*, 1959, **36**, 659). In this communication are described the preparations of 2-(*m*-methyl-, *p*-methyl-, 2 : 4- and 2 : 5-dimethyl-, *p*-methoxy-, *o*- and *m*-bromo-) benzylimino-4 thiazolidones and their condensation products with various aldehydes.

Experimental

The preparation of 2-benzylimino-4-thiazolidones and their condensation with aldehydes were carried out as described earlier (Trivedi *et al.*, *loc. cit.*). 2-Benzylimino-4-thiazolidones and their condensation products with aldehydes are listed in Tables I and II respectively.

Table I

2-Benzylimino-4-thiazolidones.



[T represents -benzylimino-4-thiazolidone]

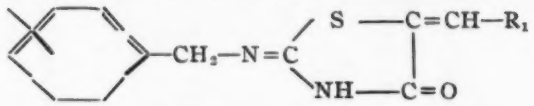
No.	Compounds.	M.P.	Formula.	% Nitrogen. Found.	Calc.
1.	2-*m*-Methyl-T	210°	$C_{11}H_{12}ON_2S$	12.4	12.7
2.	2-*p*-Methyl-T	228°	$C_{11}H_{12}ON_2S$	12.5	12.7
3.	2-(2 : 4-Dimethyl)-T (shining plates from dil. alcohol)	183°	$C_{12}H_{14}ON_2S$	11.9	12.0
4.	2-(2 :5-Dimethyl)-T (colorless needles from dil.alcohol)	176°	$C_{12}H_{14}ON_2S$	11.8	12.0
5.	2-*p*-Methoxy-T	218°	$C_{11}H_{12}O_2N_2S$	11.8	11.9
6.	2-*o*-Bromo-T	209°	$C_{10}H_9ON_2BrS$	9.5	9.8
7.	2-*m*-Bromo-T (white plates from dil. alcohol)	161°	$C_{10}H_9ON_2BrS$	9.7	9.8

The authors thank Dr. R. D. Desai for interest in the work, the Ahmedabad Education Society for defraying the expenses incurrred during the course of this work and the Govt. of India for a grant to J. J. T.

Compounds 1, 2, 5 and 6 could not be crystallised from common solvents because of their much less solubility. These were repeatedly washe l with hot water and dried.

TABLE II

R 5 *Benzylidene-2-benzylimino-4-thiazolidones.*



No	Compounds.	* Cryst. shape.	M.P.	Formula.	% Nitrogen. Found.	Calc.
1.	5-Benzylidene-2-*m*-methylbenzylimino-T**	Yellow grains	189°	$C_{18}H_{16}ON_2S$	8.8	9 1
2.	5-(4-Methoxybenzylidene)-2-*m*-methylbenzylimino-T	Yello·v plates	195°	$C_{19}H_{18}O_2N_2S$	7.9	8.3
3.	5-(2-Chlorobenzylidene)- Do	Yellow grains	148°	$C_{18}H_{15}ON_2ClS$	8.0	8.2
4	5-(4-Chlorobenzylidene)- Do	Yellow grains	234°	$C_{18}H_{15}ON_2ClS$	7.8	8.2
5.	5-Benzylidene 2-*p*-methylbenzylimino-T	Light yellow grains	174°	$C_{18}H_{16}ON_2S$	8 9	9.1
6.	5-(4-Methoxybenzylidene)-2-*p*-methylbenzylimino-T	Reddish yellow grains	185°	$C_{19}H_{18}O_2N_2S$	8.2	8.3
7.	5-(2-Chlorobenzylidene)- Do	Yellow grains	190°	$C_{18}H_{15}ON_2ClS$	8.0	8.2
8.	5-(4-Chlorobenzylidene)- Do	Yellow plates	221°	$C_{18}H_{15}ON_2ClS$	7.8	8 2
9.	5-(3 :4-Dichlorobenzylidene)- Do	Yellow grains	236°	$C_{18}H_{14}ON_2Cl_2S$	7.1	7.4
10.	5-Benzylidene-2-(2 :4-dimethylbenzyl)-imino-T	Light yellow plates	158°	$C_{19}H_{18}ON_2S$	8 3	8.7
11.	5-(4-Methoxybenzylidene)- Do	Reddish yellow needles	164°	$C_{20}H_{20}O_2N_2S$	7.7	8.0
12.	5-(2-Chlorobenzylidene)- Do	Yellow plates	168°	$C_{19}H_{17}ON_2ClS$	7.6	7.8
13.	5-(4- Do)- Do	Yellow grains	196°	$C_{19}H_{17}ON_2ClS$	7.5	7.8
14.	5-(3 :4-Dichloro- Do) Do	Yellow grains	225°	$C_{19}H_{16}ON_2Cl_2S$	7.0	7.2
15.	5-Benzylidene-2-(2 :5-dimethylbenzyl)-imino-T	Light yellow grains	232°	$C_{19}H_{18}ON_2S$	8.4	8.7
16.	5-(4-Methoxybenzylidene)-2(2 :5-dimethylbenzyl)-imino-T	Reddish yellow grains	205°	$C_{20}H_{20}O_2N_2S$	7 9	8.0
17.	5-(2-Chloro- Do) Do	Piates	231°	$C_{19}H_{17}ON_2ClS$	7.7	7.8
18.	5-(4-Chloro- Do) Do	White grains	210°	$C_{19}H_{17}ON_2ClS$	7.6	7.8
19	5-(3 :4-Dichloro- Do) Do	Needles	238°	$C_{19}H_{16}ON_2Cl_2S$	6 8	7.2
20.	5-Benzylidene-2-*p*-methoxybenzylimino-T	Needles	183°	$C_{18}H_{16}O_2N_2S$	8.3	8.6
21	5-(4-Methoxybenzylidene)-2-*p*-methoxylbenzylimino-T	Yellow grains	132°	$C_{19}H_{18}O_3N_2S$	7.6	7.8
22.	5-(2-Chlorobenzylidene)- Do	Light yellow grains	206°	$C_{18}H_{15}O_2N_2ClS$	7.5	7 8
23.	5-(4-Chloro- Do) Do	Plates	220°	$C_{18}H_{15}O_2N_2ClS$	7.7	7 8
24.	5-(3 :4-Dichloro-Do) Do	Light yellow grains	178°	$C_{18}H_{14}O_2N_2Cl_2S$	7.1	7.1
25.	5-Benzylidene-2-*o*-bromobenzylimino-T	Plates	146°	$C_{17}H_{13}ON_2BrS$	7.2	7.5
26.	5-(4-Methoxybenzylidene)-2-*o*-bromobenzylimino-T	Yellow grains	177°	$C_{18}H_{15}O_2N_2BrS$	6.6	6.9
27.	5-(2-Chloro- Do) Do	Light yellow grains	179°	$C_{17}H_{12}ON_2BrClS$	6.7	6.9
28.	5-(4-Chloro- Do) Do	Plates	177°	$C_{17}H_{12}ON_2BrClS$	6.8	6 9
29.	5-(3 :4-Dichloro- Do) Do	Plates	180°	$C_{17}H_{11}ON_2Cl_2BrS$	6.1	6.3
30.	5-Benzylidene-2-*m*-bromobenzylimino-T	Light brown plates	203°	$C_{17}H_{13}ON_2BrS$	7 3	7.5
31.	5-(4-Methoxybenzylidene)- Do	Orange grains	194°	$C_{18}H_{15}O_2N_2BrS$	6.8	6.9
32.	5-(2-Chlorobenzylidene)- Do	Plates	208°	$C_{17}H_{12}ON_2ClBrS$	6.6	6 9
33.	5-(4-Chloro- Do) Do	Yellow plates	226°	$C_{17}H_{12}ON_2BrClS$	6.7	6.9

**T denotes 4-thiazolidone

* From acetic acid

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Received April 17, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

Received April 17, 1959.

THIAZOLIDONES. PART III. SYNTHESIS OF 2-ARYLIMINO-5-ARYL-4 THIAZOLIDONES

By B. K. Raval and J. J. Trivedi

α-Bromophenyl- and α-bromo-*o*-chlorophenyl-acetic acids have been condensed with phenylthioureas to obtain 2-phenylimino-5-phenyl- (and 5-*o*-chlorophenyl)-4-thiazolidones.

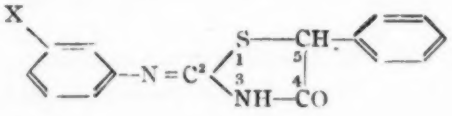
In the case of rhodanines, which are related to thiazolidones, Bradsher *et al.* (*J. Amer. Chem. Soc.*, 1956, **78**, 384) observed that 3-phenylrhodanines were superior to 3-benzylrhodanines in activity towards *A. niger*, while with reference to bactericidal activity towards *B. subtilis* and *E. coli*, the latter were more active. Thiazolidones, having phenyl and benzyl groups on C_5, do not seem to have been studied. It was therefore planned to synthesise thiazolidones containing phenyl and benzyl groups on C_5 position. In this communication are described 2-substituted phenylimino-5-phenyl- and -5-(*o*-chlorophenyl)-4-thiazolidones.

Substituted phenylthioureas were prepared from the corresponding amines. α-Bromophenylacetic acids were prepared from the corresponding mandelic acids by the method used by Bruce and Sutcliffe (*J. Chem. Soc.*, 1957, 4793). The mandelic acids were prepared from the corresponding aldehydes by the method used by Jenkins (*J. Amer. Chem. Soc.*, 1931, **53**, 2341).

Condensation of thioureas with α-bromophenylacetic acids was carried out as described by Rylander and Campaigne (*J. Org. Chem.*, 1950, **15**, 252) and Rout and Mahapatra (*J. Amer. Chem. Soc.*, 1955, **77**, 2428). Thiazolidones (yield more than 60%), were crystallised from alcohol. The compounds are described in Tables I and II.

TABLE I

2-Substituted phenylimino-5-phenyl-4-thiazolidones.



No.	X.	M.P.	Formula.	% Sulphur. Found.	Calc.	No.	X.	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	306°	$C_{15}H_{12}ON_2S$	12.1	11.9	9	*o*-OMe	170°	$C_{16}H_{14}O_2N_2S$	10.5	10.7
2.	*o*-Cl	280°	$C_{15}H_{11}ON_2ClS$	10.4	10.6	10.	*p*-OMe	225°	,,	10 9	,,
3.	*m*-Cl	175°	,,	10.5	,,	11.	2 :4-Di-Cl	160°	$C_{15}H_{10}ON_2Cl_2S$	9.6	9 5
4.	*p*-Cl	180°	,,	10.6	,,	12.	2 :5-Di-Cl	160°	,,	9·7	,,
5.	*p*-Br	190°	$C_{15}H_{11}ON_2BrS$	9.0	9.2	13.	3 :4-Di-Cl	210°	,,	9.8	,,
6.	*o*-Me	200°	$C_{16}H_{14}ON_2S$	11·5	11.3	14.	*o*-CO_2Et	185°	$C_{18}H_{16}O_3N_2S$	9 6	9.4
7.	*m*-Me	130°	,	11.4	,,	15.	*p*-OEt	190°	$C_{17}H_{16}O_2N_2S$	10 6	10 3
8.	*p*-Me	188°	,,	11.1	,,	16.	*p*-*n*-OPr	160°	$C_{18}H_{1_3}O_2N_2S$	10.0	9.8
						17.	*p*-*n*-OC_6H_{13}	150°	$C_{21}H_{24}O_2N_2S$	8.8	8.7

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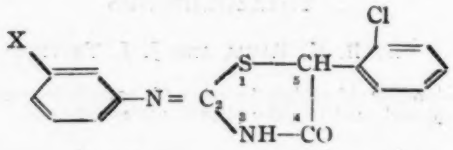
TABLE II

2-Substituted phenylimino-5-(o-chlorophenyl)-4-thiazolidones.



No.	X.	M.P.	Formula.	% Sulphur. Found.	Calc.	No.	X.	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	203°	$C_{15}H_{11}ON_2ClS$	10.4	10.6	8.	*p*-OMe	170°	$C_{16}H_{13}O_2N_2ClS$	9.8	9.6
2.	*m*-Cl	170°	$C_{15}H_{10}ON_2Cl_2S$	9.7	9.5	9.	2 :4-Di-Cl	145°	$C_{15}H_9ON_2Cl_3S$	8.9	8.6
3.	*p*-Cl	204°	,,	9.8	,,	10.	2 :5-Di-Cl	138°	,,	8.7	,,
4.	*p*-Br	214°	$C_{15}H_{10}ON_2ClBrS$	8.2	8.4	11.	3 :4-Di-Cl	08°	,,	8.6	,,
5.	*o*-Me	147°	$C_{16}H_{13}ON_2ClS$	10.0	10.1	12.	*o*-CO_2Et	194°	$C_{18}H_{15}O_3N_2ClS$	8.4	8.5
6.	*m*-Me	162°	,,	9.8	,,	13.	*p*-*n*-OPr	188°	$C_{18}H_{17}O_2N_2ClS$	8.6	8.9
7.	*p*-Me	211°	,,	10.4	,,	14.	*p*-*n*-OBu	171°	$C_{19}H_{19}O_2N_2ClS$	8.4	8.5

Patnaik and Pujari (this *Journal*, 1957, **34**, 814) record m.p.s of the compounds No. 1, 3 and 4 as 154°, 161° and 267° respectively.

The authors thank Dr. R. D. Desai for interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work.

CHEMISTRY DEPARTMENT,
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Received April 30, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

ESTIMATION OF NICKEL AND PALLADIUM BY αβ-DIOXIMINOACETOACET-*o*-TOLUIDIDE

By J. S. Dave and A. M. Talati

αβ-Dioximinoacetoacet-*o*-toluidide quantitatively precipitates nickel and palladium as $M(C_{22}H_{24}O_6N_6)$ (M=Ni or Pd), the former at *p*H 5.1–9.1 and the latter at *p*H 0.1-10.0. The effect of ions on the estimation of Ni and Pd by this reagent has also been studied.

In continuation of our previous communications (this *Journal*, 1959, **36**, 179, 302) we present herein our studies on the gravimetric estimation of nickel and palladium by αβ-dioximinoacetoacet-*o*-toluidide. Nickel and palladium form with αβ-dioximinoacetoacet-*o* toluidide respectively an orange and a yellow complex which are formulated as $M(C_{11}H_{12}O_3N_3)_2$ (where M=Ni or Pd). Nickel is quantitatively precipitated by this reagent within the *p*H range 5.1 to 9.1. Various anions and cations (studied herein) do not interfere with the estimation of nickel by this reagent under prescribed conditions.

Palladium is quantitatively precipitated from fairly acidic solutions (*p*H 0.4), under which conditions no other metal complex of this reagent is precipitated. Mercury (ic), tin (ous), zinc, manganese, cobalt, nickel, copper, chromium, antimony, calcium, strontium, barium and magnesium do not interfere under the experimental conditions. It has been observed, however, that an error is introduced when nitrate ion is present.

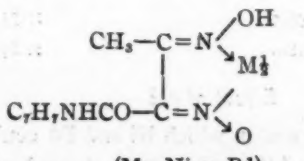
Experimental

αβ-Dioximinoacetoacet-*o*-toluidide was prepared from acetoacet-*o*-toluidide (Dave and Talati, *Curr. Sci.*, 1957, **26**, 326); 1% alcoholic solution of this reagent was used for all estimations. Solutions of chlorides of Ni and Pd and other reagents were the same (*loc.cit.*).

Composition of the Complexes.—The nickel and palladium complexes of the reagent were prepared and their composition was determined, as discussed in the previous communication (*loc.cit.*).

[Found: Ni (DMG), 11.08, 11.19. Calc. for Ni $(C_{22}H_{24}O_6N_6)$: Ni, 11.13%]. [Found: Pd (ignition), 18.58, 18.56. Calc. for Pd $(C_{22}H_{24}O_6N_6)$: Pd, 18.55%].

The results suggest the composition of the complexes as $M(C_{11}H_{12}O_3N_3)_2$ which may be represented as



(M=Ni or Pd)

Analytical Procedure

Nickel.—An aliquot quantity of nickel chloride solution was diluted to about 200 c.c. with distilled water. To the warm solution was added a sufficient amount of the reagent solution (1 g. reagent solution for 0.09 g. Ni) and the *p*H of the solution was adjusted to 7-8. The orange precipitates obtained were digested on the water-bath for about an hour. The precipitates were filtered through a sintered glass crucible or quantitative filter paper, washed with water and dried at 110-20° to a constant weight and weighed as $Ni(C_{11}H_{12}O_3N_3)_2$, the factor for nickel being 0.1113. Some of the results are recorded in Table I.

TABLE I

Ni taken.	Salt added.		Ni complex.	Ni found	Error.
6.81 mg.	...		61.00 mg.	6.79 mg.	− 0.02 mg.
13.22	...	...	118.7	13.21	− 0.01
6.81	$MgCl_2$,	0.500 g.	61.7	6.87	+ 0.06
6.81	$ZnSO_4$	0.143	61.6	6.86	+ 0.05
6.81	$HgCl_2$,	0.136	61.2	6.81	± 0.00
13.22	$CdSO_4$,	0.064	118.3	13.17	− 0.05
6.81	$CaCl_2$,	0.550	61.4	6.83	+ 0.02
6.81	$Sr(NO_3)_2$,	0.650	60.7	6.76	− 0.05
6.81	KBr,	2.000	61.9	6.89	+ 0.08
6.81	KI,	2.000	62.1	6.91	+ 0.10
6.81	$NaNO_3$,	2.000	61.7	6.87	+ 0.06

Palladium.—An aliquot quantity of palladium solution was diluted to about 200 c. c. with dilute HCl solution (*p*H adjusted to 0.4 − 0.7). To this solution was added, after warming, 1% alcoholic solution of the reagent (1 g. reagent for 0.1 g. Pd). The flocculent precipitates obtained were digested on the water-bath for about an hour. The precipitates were filtered through a quantitative filter paper or sintered glass crucible, washed with water and dried at 110-20° to a constant weight and weighed as Pd $(C_{22}H_{24}O_6N_6)$, the factor for Pd being 0.1855. Some of the results are recorded in Table II.

TABLE II

Pd taken.	Pd complex.	Pd found.	Error.
4.44 mg.	24.1 mg.	4.47 mg.	+ 0.03 mg.
8.62	46.7	8.66	+ 0.04
11.40	62.0	11.50	+ 0.10
17.24	93.4	17.33	+ 0.09
21.94	118.0	21.89	− 0.05

Effect of pH

In order to study the *p*H range within which Ni and Pd could be completely precipitated by this reagent, estimations of the metals were carried out in solutions having

different *p*H values. *p*H values of the undiluted filtrates of each were determined by L and N *p*H meter. The results are recorded in Tables III and IV, which show that nickel is completely precipitated by this reagent within *p*H 5 1 to 9.1 and palladium, above *p*H 0.1 (and at least up to *p*H 10.0).

TABLE III

Ni taken = 13.22 mg.

*p*H	4.6	5.06	6.98	9.10
Ni found (mg)	12.15	13.21	13.27	13.22

TABLE IV

Pd taken.	*p*H.	Pd complex.	Pd found.
11.40 mg.	0.12	62.0 mg.	11.50
8.62	0.40	46.7	8.66
8.62	0.60	46.7	8.66
8.62	5.42	46.5	8.63
11.40	10.00	61.2	11.35

Effect of Anions and Cations

Nickel was estimated by this reagent at *p*H 7 to 8 and palladium at 0.4–0.7 in presence of different cations and anions. In case of the latter, precipitates were washed twice with dilute HCl and then with water. The results, as presented in Table I and in Table V, indicate little or no interference by the ions studied.

TABLE V

Pd taken.		Salt added.			Pd complex.	Pd found.	Error.
8.62 mg.		$SnCl_2$,	0.113 g.		46.7 mg.	8.66 mg.	+ 0.04 mg.
11.40		$HgCl_2$,	0.136		61.4	11.39	− 0.01
8.62		$SbCl_3$,	0.113		46.4	8.61	− 0.01
8.62		$ZnSO_4$,	1.430		46.4	8.61	− 0.01
8.62		$MnCl_2$,	0.099		46.3	8.59	− 0.03
8.62		$CoCl_2$,	0.119		46.9	8.70	+ 0.08
8.62		$CrCl_3$,	0.134		47.2	8.76	+ 0.14
11.40		$CaCl_2$,	1 100		62.0	11 50	+ 0.10
11.40		$BaCl_2$,	1.500		61.8	11.46	+ 0.06
11.40		$MgCl_2$,	0.500		62.4	11 58	+ 0.18
5.87		$NiCl_2$,	13.22 mg.	(Ni)	31.5	5.84	− 0.03
11.40		$NiCl_2$,	13.22	(Ni)	61.8	11.46	+ 0.06
5.87	*p*H.	$CuCl_2$,	7.85	(Cu)	31.7	5.88	+ 0.01
11.40	1.90	$NaNO_3$,	2 g.		66.6	12.35	+ 0.95
11.40	2.62	K_2SO_4,	2		61.9	11.48	+ 0.08
11.40	8.28	KBr,	2		62.0	11.50	+ 0.10
11.40	8.94	KI,	2		61.9	11.48	+ 0.08
8.62	9.40	$NaNO_3$,	2		49.7	9.22	+ 0.60

Similarly the estimation of palladium was carried out in presence of different anions at different *p*H values and the results are recorded in Table V. The results indicate that bromide and iodide ions cause no interference when the estimation is carried out from alkaline solutions, and that nitrate ion does interfere both in acidic and alkaline solutions.

Thanks of the authors are due to Dr. B. N. Mankad and Prof. S. M. Sethna for their continued interest in the work.

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Received June 15, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

PREPARATION OF URANIUM(IV) OXYACETATE AND TETRA-ACETATE

By K. K. Tripathy, Balaram Sahoo and D. Patnaik

Uranium(IV) oxyacetate has been prepared by the photochemical reduction of uranyl acetate in a mixture of acetic anhydride and alcohol. The compound obtained is a dirty green fine powder and possesses the formula $UO(CH_3COO)_2.H_2O$. When this aquo-oxyacetate is refluxed with acetic anhydride, anhydrous uranium(IV) tetra-acetate, $U(CH_3COO)_4$, is obtained.

The photolysis of uranyl ion in presence of different anions has been extensively investigated in this laboratory, and several compounds, namely, uranium(IV) oxyformate (Sahoo and Patnaik, *Curr. Sci.*, 1958, **27**, 243), oxyoxalate and oxalate (Patnaik and Sahoo, *ibid.*, 1958, **27**, 292), oxysulphate (Sahoo and Patnaik, this *Journal*, 1959, **36**, 483), tetrafluoride (Patnaik and Sahoo, *Proc. Ind. Acad. Sci*, 1959, **49A**, 200) and the complex $NH_4F.UF_4.H_2O$ (Sahoo and Patnaik, *Curr. Sci.*, 1959, **28**, 195) have been prepared. Further, these compounds have assumed importance on account of the fact that these lead to a convenient method for the preparation of uranium dioxide (*ibid.*, 1959, **28**, 364) and uranium tetrafluoride (Sahoo and Patnaik, *ibid.*, 1959, **28**, 16) and for the photolytic separation of uranium from other associated elements (unpublished) in the pure state. Study of these observations led us to attempt to prepare anhydrous uranium^{IV} tetra-acetate, which would be the most suitable compound for the preparation of anhydrous uranium tetrafluoride. Rosenheim and Kelmy (*Z. anorg. allgem. Chem.*, 1932, **206**, 31) prepared the tetra-acetate by refluxing uranium (IV) tetrachloride with acetic acid. We attempted to prepare the same photolytically by the application of solar energy. When photolysis of UO_2^{2+} ion is brought about in presence of CH_3COO^- ion, $UO(CH_3CO_2)_2.H_2O$ is obtained instead of $U(CH_3CO_2)_4$.

Experimental

Uranyl nitrate, acetic acid and acetic anhydride used were of E. Merck quality. Acetate was prepared from the nitrate by the action of acetic acid. Uranyl acetate (5 g.), dissolved in water (40-50 c.c.), was mixed with an equal volume of acetic anhydride and absolute alcohol, and exposed to sunlight. Reduction of U^{6+} to U^{4+} occurred with the precipitation of a dirty green solid in about half an hour. On further exposure, more of the compound was formed and settled down. The supernatant liquid was decanted off, washed with absolute alcohol for several times and dried in vacuum at room temperature for 24 hours.

The molecular weight of the compound was determined from the U_3O_8, obtained by heating a weighed quantity of the compound in a platinum crucible. Uranium (IV) content was determined by direct titration with $KMnO_4$. Acetate was determined by the method of hydrolysis. Total hydrogen and carbon were determined by the semimicro combustion method. The analytical data recorded in Tables I-III show the compound to be aquo-oxyacetate having the formula $UO(CH_3CO_2)_2.H_2O$.

TABLE I

Mol. formula : $UO(CH_3CO_2)_2.H_2O$.

Compound taken.	U_3O_8 obtained.	Mol. wt. Found.	Calc.
127.7 mg.	91.8 mg.	390.4	390
189.3	136.2	390.2	
201.8	144.9	390.8	
234.5	168.5	390.5	

TABLE II

Estimation of uranium and acetate.

Compound taken.	Uranium Found.	Calc.	Compound taken.	Acetate Found.	Calc.
204.4 mg.	124.6 mg.	124.8 mg.	113.7 mg.	34.8 mg.	34.4 mg.
208.3	127.2	127.2	177.5	54.1	53.7
224.9	137.0	137.2	221.8	67.6	67.1
256.1	156.0	156.3	257.5	78.7	77.9

TABLE III

Estimation of carbon and hydrogen.

Compound taken.	Water. Found.	Calc.	Carbon dioxide. Found.	Calc.	% Hydrogen. Found.	Calc.	% Carbon. Found.	Calc.
55.7 mg.	10.5 mg.	10.28 g.	24.7 mg.	25.14 mg.	2.094	2.05	12.09	12.31
70.1	13.1	12.94	31.4	31.63	2.076	,,	12.22	,,

With a view to obtaining the anhydrous oxyacetate, the hydrated compound was heated at 130°, when partial decomposition and oxidation occurred. This hydrated compound (5 g.) was refluxed with acetic anhydride (100 c c.) for a period of 2 hours, after which, it was filtered and dried in vacuum as mentioned above. The analysis of the compound was carried out exactly in the same manner as the oxyacetate. The results of analysis, recorded in Tables IV-VI, show the compound to be anhydrous uranium tetra-acetate $U(CH_3CO_2)_4$.

TABLE IV

Mol. formula : $U(CH_3COO)_4$.

Compound taken.	U_3O_8 obtained.	Mol. wt. Found.	Calc.
144.7 mg.	85.9 mg.	472.9	474
164.8	97.7	473.4	
188.3	111.9	472.5	
203.8	121.2	472.0	

TABLE V

Estimation of uranium and acetate.

Compound.	Uranium.		Compound	Acetate.	
taken.	Found.	Calc.	taken.	Found.	Calc.
159.8 mg.	100.0 mg.	100.3 mg.	179.9 mg.	90.4 mg.	89.6 mg.
218.7	110.1	109.8	207.7	104.5	103.4
222.6	111.8	111.8	211.3	105.9	105.2
244.0	122.9	122.6	287.6	144.6	143.2

TABLE VI

Estimation of carbon and hydrogen.

Compound	Water		Carbon dioxide.		% Hydrogen.		% Carbon.	
taken.	Found.	Calc.	Found	Calc.	Found.	Calc.	Found.	Calc.
32.8 mg.	7.5 mg	7.47 mg.	24.2 mg.	24.35 g.	2.54	2.53	20.12	20.25
50.5	11.7	11.50	37.1	37.50	2.57	,,	20.04	,,

The anhydrous complex $NH_4F.UF_4$ has been prepared by heating an intimate mixture of anhydrous uranium (IV) tetra-acetate and ammonium bifluoride $NH_4F.HF$ (1 : 6) in vacuum at about 250°. The thermal decomposition of this anhydrous complex produces anhydrous uranium tetrafluoride, which will be described in a separate communication.

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Received May 25, 1959

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

SHORT NOTES

DICYANOETHYLATION OF 9-AMINOFLUORENE

By Thomas George and P. I. Ittyerah

Braunholtz and Mann (*J. Chem. Soc.*, 1952, 3046 ; 1953, 1817 ; 1954, 651) have described a very elegant method for the dicyanoethylation of aromatic primary amines. In this communication is described the dicyanoethylation of 9-aminofluorene and the subsequent hydrolysis of the dicyanoethyl derivative.

9-Aminofluorene was prepared from fluorene ; the latter was converted to fluorenone by oxidation with glacial acetic acid and sodium dichromate (Huntress *et al.*, *J. Amer. Chem. Soc.*, 1931, **53**, 2721). The oxime of the ketone was then prepared in the usual manner (Spiegler, *Monatsh.*, 1884, **5**, 195 ; Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 2621) and reduced with zinc dust and alcohol to yield the amine (Ingold and Wilson, *J. Chem. Soc.*, 1933, 1499).

Dicyanoethylation of 9-Aminofluorene: Formation of NN-bis-2′-*Cyanoethyl-9-aminofluorene.*—9-Aminofluorene (10 g.), acrylonitrile (7.5 g.), acetic acid (8 g.) and cuprous chloride (0.5 g.) were mixed and gently refluxed for 12 hours. The resulting solution was poured into liquor ammonia and stirred well. The solid product was filtered, washed several times with water and recrystallised from alcohol, m.p. 105°, yield 6 g. (Found : N, 14.97. $C_{19}H_{17}N_3$ requires N, 14.63%). The compound did not respond to any of the usual tests for a primary or a secondary amino group. Examination of the infra-red spectrum of the compound also did not show any evidence for the presence of a primary or a secondary amino group.

Hydrolysis of NN-bis-2′-*Cyanoethyl-9-aminofluorene : Formation of* NN-bis-(2′-*Carbethoxy*)-9-*aminofluorene and its Hydrochloride.*—*NN-bis-*2′-Cyanoethyl-9-aminofluorene (1.5 g.), KOH (1.5 g.) and alcohol (17 c.c.) were mixed in a flask and refluxed for 2 hours. The resulting solution was warmed in an open porcelain dish to drive off a part of the alcohol. It was acidified with HCl (conc.). *NN-bis-*(2′-Carbethoxy)-9-aminofluorene hydrochloride crystallised out. This was filtered and washed well with acetone, m.p. 192°. (Found : N, 4.21. $C_{19}H_{20}O_4NCl$ requires N, 3.87%).

The above hydrochloride on recrystallisation from water resulted in the splitting off of hydrogen chloride and the formation of *NN-bis-*(2′-carbethoxy)-9-aminofluorene, m.p. 162°. (Found : Equiv., 161.7. Calc. equiv., 162.5).

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Received August 22, 1959.

[Jour. Indian Chem. Soc., Vol. 36, No. 10, 1959]

SHORT NOTES

INTERFERENCE CORRECTIONS

By A. M. Talati

Gibling (*J. Chem. Soc.*, 1941, 299, 306 et seq) suggested different values of the interference correction (I.C.) for the groupings C—C—X, where X = C, N, O or S. The present author (this *Journal*, 1955, **32**, 471; 799; 1956, **33**, 301) found that the values of I.C. for the groupings C—C—X, where X = C, N or O, are the same, namely, 2.2 and that for C—C—Cl is zero. In the present communication, the values of I.C. for the groupings: C—C—Br, C—C—I and C—C—S have been derived and the interference effect in the groupings C—C—X, where X = C, N, O, S, Cl, Br or I, has been discussed.

The group parachor values of the groups: (C) CH_2Br, $(C)_2CHBr$, $(C)CH_2I$, $(C)_2CHI$, $(C)CH_2SH$, $(C)_2CHSH$ and $(C)_3CSH$ are calculated from the mean of the known parachor values (observed) of ethyl bromide, propyl^i bromide, ethyl iodide, propyl^i iodide, ethyl mercaptan, propyl^i mercaptan and butyl^t mercaptan respectively. These values are recorded in Table I along with those for alkyl groups for correlation.

TABLE I

		X = Br		X = I		X = SH		X = H	
	Group.	$(P)_{calc.}$	Diff.	$(P)_{calc.}$	Diff.	$(P)_{calc.}$	Diff.	$(P)_{calc.}$	Diff.
(i)	$(C)CH_2X$	110.1	...	131.5	...	107.0	...	55.2	...
(ii)	$(C)_2CHX$	94.7	15.4	116.1	15.4	91.6	15.4	39.8	15.4
(iii)	$(C)_3CX$	...	...	...	...	74.0	17.6	22.2	17.6

From the table the same difference of 15.4 is observed between (*i*) and (*ii*) and a constant difference of 17.6 is observed between (*ii*) and (*iii*). These results suggest that in these groups Br, I and S atoms resemble H atom as regards interference caused by these atoms, *i.e.*, the values of I.C. for the groupings C—C—X will be zero if the values of I.C. for the groupings H—C—X (X = Br, I or S) are taken as zero and the parachor value of H is taken as 13.2 in all the cases. The ideal R.P. values for the groups: $(C)CH_2Br$, $(C)_2CHBr$, $(C)CH_2I$, $(C)_2CHI$, $(C)CH_2SH$, $(C)_2CHSH$ and $(C)_3CSH$ will then be 110.1, 96.9, 131.5, 118.3, 107.0, 93.8 and 80.6 respectively. The group parachor values for the groups $(C)_3CBr$ and $(C)_3CI$ are 77.1 and 98.5 and their ideal R.P. values are 83.7 and 105.1 respectively.

Gibling did not suggest anything about I.C. for the groupings C—C—Br and C—C—I. Although he suggested a value of I.C for C—C—S as 2.7, he calculated it from a single group parachor value, and not by this method.

We can now consider the interference effect in the groupings C—C—X, where X = C, N, O, S, Cl, Br, I or H. From Gibling's values of I.C. for different groupings (C—C—X), it is apparent that the nature of the atom has an important bearing on the interference effect. Thus, when X is an atom of an element of the same

period as that of carbon in the Periodic Table, the value of I.C. increases as the radius of the atom decreases; when atoms (X) of the same group are considered, the value of I.C. for C—C—X increases as the size of the atom is increased. It is found from our values, however, that in such a grouping (C—C—X), elements of the same period behave similarly as regards interference. Thus, the value of I.C. for C—C—X is 2.2 when X = C, N or O and zero, when X = S or Cl. Further, it is observed that if X is an atom of an element of a period different from that of carbon, the value of I.C. is zero. Thus, a relatively "large" atom like that of S, Cl, Br or I and 'very small" H atom produce zero interference in the grouping C—C—X.

The same value of I.C. for the grouping C—C—X, where X = C, N or O, may be explained qualitatively as follows. In the groupings:

and

the interfering distances between the non-linked atoms are in the order: (C C'') > (C N) > (CO), exhibiting an apparent variation in the values of I.C. for these groupings. This variation may be considered, however, to be counterbalanced by the change in the size of the non-linked atoms.

The author expresses his gratefulness to Principal M. D. Avasare, Prof. S. M. Sethna and Dr. J. S. Dave for their interest in the work.

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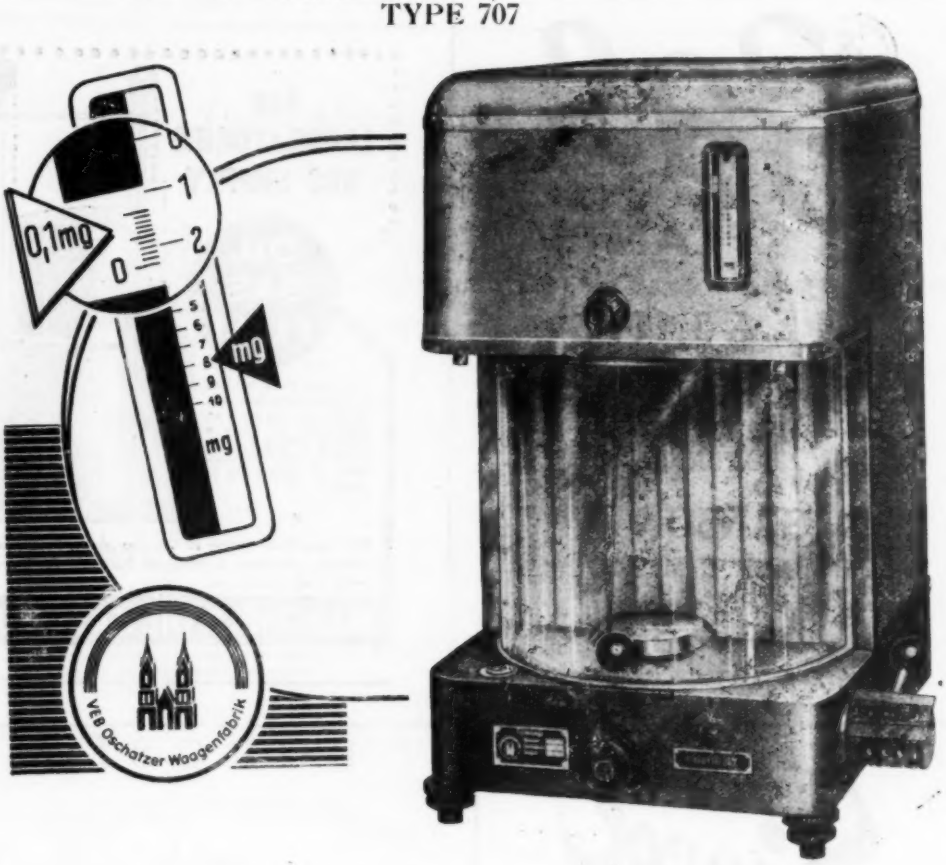

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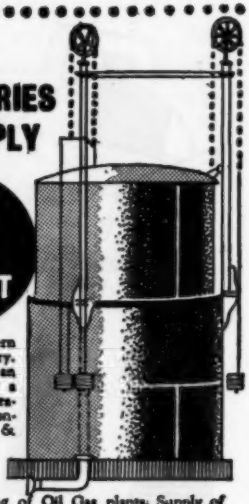

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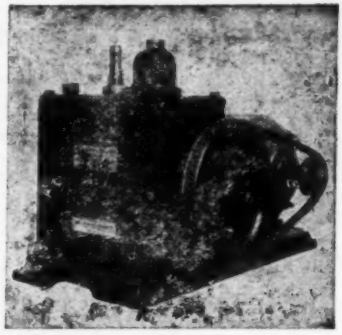

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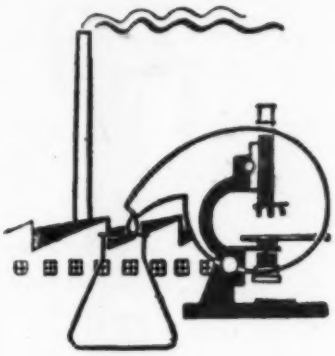

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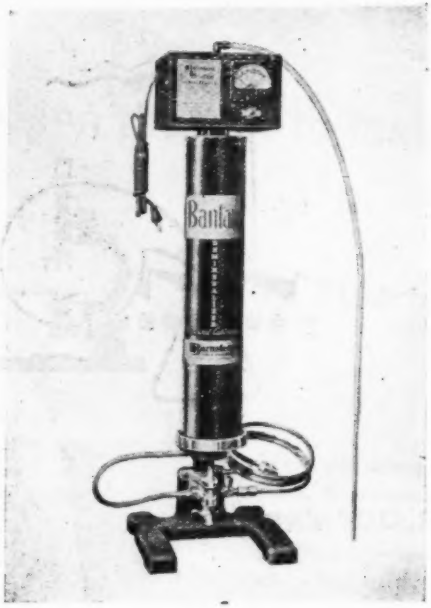

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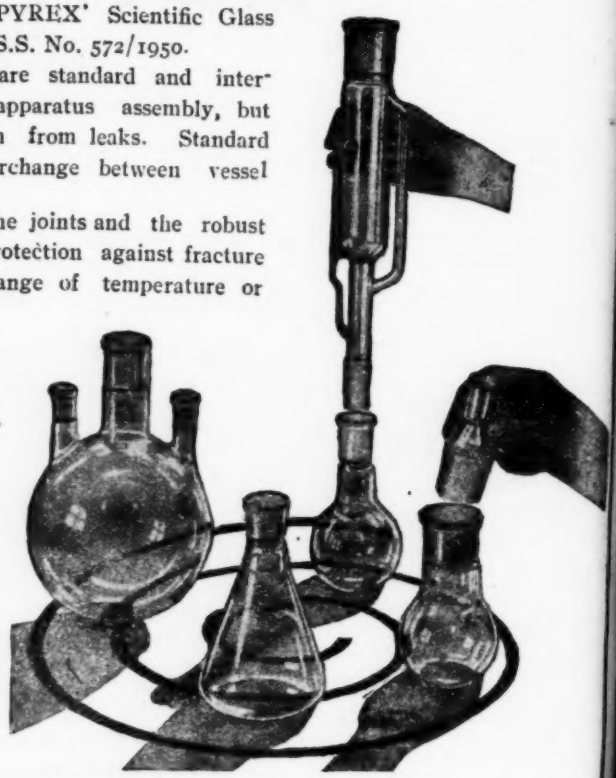

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Printed by Sri Sibendranath Kanjilal, Superintendent, Calcutta University Press, 48, Hazra Road, Ballygunge, Calcutta and Published by .G Banerjee, M.Sc., Asst. Editor, Indian Chemical Society.